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Experimental High-Throughput Adsorption Unit for Multi-Evaluation of Adsorbents for Gas Capture, Storage and Separation Applications

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“The literature pertaining to the sorption of gases by solids is now so vast that it is impossible for any, except those who are specialists in the experimental technique, rightly to appraise the work, which has been done, or to understand the main theoretical problems which require elucidation.” J. E. Lennard-Jones, 1932

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O meu mais sincero obrigado a todos.

João Gomes

RESUMO

Nesta tese, foi projectada e construída uma unidade experimental para a medição de dados de equilíbrio de adsorção através do método volumétrico. Esta unidade permite a realização de experiências simultâneas, de modo a obter equilíbrios de adsorção de uma forma rápida e eficiente.

Foi também criada a respectiva interface para aquisição e controlo. Esta interface foi desenvolvida em LabVIEW e visa monitorizar as variáveis do sistema, controlar as funções das válvulas solenóides presentes na unidade e registar para posterior análise os dados experimentais obtidos.

Em seguida, procedeu-se a uma calibração dos volumes da instalação, para posterior utilização nos cálculos do referido método.

Seguidamente procedeu-se à validação experimental da unidade. Para a validação foram seleccionados dois materiais porosos previamente estudados pelo método de adsorção gravimétrico: um carvão activado, ANGUARD 5 (Suttclife Speakman, Reino Unido) e um *metal-organic framework* (MOF) MIL-53(Al) (Basolite A100®, BASF SE, Alemanha). Dois gases com elevado potencial de separação e armazenamento foram escolhidos: Dióxido de Carbono (CO_2) e Azoto (N_2). A unidade é composta por duas linhas independentes pelo que os ensaios em ambos os materiais foram realizados em simultâneo.

Foram realizados ensaios a diferentes temperaturas e diferentes intervalos de pressão para ambos os materiais. Foram realizados ensaios de CO_2 em ambos os materiais a 30ºC, 80ºC e 150ºC. Para o primeiro, o intervalo de pressão foi entre 0 e 10 bar e para os dois últimos foi entre 0 e 15 bar. Foi realizado um ensaio de N_2 a 50ºC para ambos os materiais.

Por último, procedeu-se a uma comparação de resultados com outro método adsorptivo, o método gravimétrico. Os resultados obtidos estão em concordância com os dados obtidos por gravimetria o que mostra que a unidade construida está a funcionar correctamente. Os erros em cada medição seguiram um modelo de erro multivariável e cumulativo.

Palavras-chave: Adsorção gasosa, método volumétrico experimental, adsorventes microporosos, isotérmicas de adsorção, LabVIEW

ABSTRACT

In this thesis, an experimental unit based in the volumetric adsorption method was designed and constructed. This unit allows the realization of simultaneous experiments in order to obtain adsorption equilibria data of several adsorbents quickly and efficiently.

Following the construction of the unit, it was necessary to develop the respective interface for acquisition and control. This interface was developed using the LabVIEW software and aims to monitor the system variables, to control the functions of solenoid valves present in the unit, as well as to register the measured data for further analysis.

After the development of the interface, a volume calibration was performed.

Then the unit was ready to be experimentally validated. For this validation, two porous materials, already analysed by an adsorption gravimetric method, were selected: an activated carbon, ANGUARD 5 (Suttclife Speakman, UK) and a metal-organic framework (MOF) MIL-53 (Al) (Basolite A100 ®, BASF SE, Germany). Two gases with high potential for separation and storage were chosen for study: Carbon Dioxide (CO_2) and Nitrogen (N_2). The unit consists of two independent lines so both materials were studied simultaneously in every test.

Tests at different temperatures and for different pressure ranges for both materials were performed. CO_2 tests were performed on both materials at 30°C, 80°C and 150°C. The pressure range for the first test was between 0 and 10 bar and for the last two was between 0 and 15 bar. A test with N_2 at 50 ° C was also performed for both materials.

After, a comparison of the results obtained with other results obtained with the gravimetric method was accomplished. The results obtained are in accordance with the previously obtained gravimetric data which prove that the unit developed is working properly. The error for each measurement was obtained considering the possibility of a multivariate and cumulative error.

Keywords: Adsorption, volumetric method, isotherms, LabVIEW

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1. MOTIVATION AND OBJECTIVES

1.1 Motivation

Adsorption processes have been studied in order to present themselves as an alternative for capture, storage and separations processes. The primary objective is to find a process that can be less expensive, faster and more efficient.

Adsorption separation processes have been widely applied to many important separations in the chemical industry [1] [2]. It is currently a growing area with the development of new adsorbent materials and processes. Adsorption separation processes can be performed for raw materials purification, recovery of primary products and removal of polluting gaseous effluents, using the proper adsorbent.

The flue gas emissions from fossil fuelled power plants and also impurities in wastewater streams may contribute to a poor environmental quality being a threat to human health. Thus, as the regulatory limits on environmental emissions become more stringent, industries have developed separation technologies that could remove contaminants and pollutants from process waste streams.

Carbon Dioxide (CO_2) environmental effects have attracted substantial interest in recent years. The greenhouse effect of CO_2 associated with its increasing atmospheric concentration is accepted to have given a huge contribution to the global warming. In order to address this issue, CO_2 capture and storage have been a major research topic recently. [3] The estimation from the Intergovernmental Panel on Climate Change (IPCC) has shown that CO_2 emissions could be reduced by 80–90% for a modern power plant equipped with suitable Carbon dioxide Capture and Storage (CCS) technologies [4] [5]. The use of CCS will also complement other crucial

strategies, such as switching to low carbon-content fuels, improving energy efficiency, and phasing in the use of renewable energy resources. The two general approaches to reduce carbon emissions from existing plants are post-combustion capture and oxy-combustion. Commercial CO_2 capture technologies that exist today, such as monoethanolamine (MEA) chemical absorption, are energy intensive and, therefore expensive. Also, amine scrubbing presents corrosion problems and may cause emission of carcinogenic compounds. Adsorption becomes a viable alternative to amine scrubbing. [6] [3]. Over the years, several materials have been widely used (activated carbon, zeolites) in adsorption based separation processes. Other materials such as metal-organic frameworks have recently been studied in order to evaluate its success. Development of regenerable adsorbents that have high capacity, high selectivity and reversible adsorption of CO_2 adsorption/desorption is critical for the success of CO2 capture adsorption processes. In recent literature, it is possible to find extensive assessments in this area [7].

When it becomes necessary to study the characteristics of an adsorbent, the first measurements to be considered is the adsorption equilibrium of pure components. Therefore, it is necessary to have efficient and rapid methods to acquire data quickly and accurately. The research group, where this thesis was performed, already had an adsorption method well established (gravimetric method). The gravimetric apparatus available in the laboratory, although extremely accurate can be slow to obtain data. For that reason it was decided to develop a new apparatus (employing the volumetric method). The volumetric method is a quick and efficient method to obtain adsorption equilibrium data. Moreover, the integration of this method enables the simultaneous use of both units which can be a huge improvement for the research group efficiency in the evaluation of several adsorbents.

1.2 Objectives

The main objective of this thesis was to design and build a volumetric adsorption unit, in order to perform quick and efficient adsorption equilibrium measurements. The adsorption equilibrium of the two major components of fossil fueled power stations flue gases, CO_2 and N_2, was studied on two different adsorbents. The selected adsorbents were an activated carbon, ANGUARD 5 (Suttclife Speakman, UK) and MIL-53(Al) (Basolite A100® from BASF SE, Germany). Both adsorbents were previously tested in the gravimetric unit available in the group's laboratory. The measurements performed were compared with previously obtained data and the performance of unit built in this work could be evaluated.

2. BACKGROUND

2.1 Adsorption Phenomena

2.1.1 Basic Concepts

The term adsorption was introduced to the literature by Kayser [8] [9] in 1881 to refer to the condensation of gases on bare surfaces. Kayser also introduced the terms isotherm and isotherm curve to represent the results of adsorption experiments. In 1909, McBain [10] proposed the term sorption for adsorption and absorption in the case of phenomena which cannot be distinguished precisely.

The term adsorption is used to denote the enrichment, or accumulation, of one or more components, whether molecules, atoms or ions, in an interfacial layer between two bulk phases. In adsorption of gas-vapour/porous solid interfaces, it is customary to call the components in the adsorbed state the adsorbate, and to refer to the same species in the bulk gas phase as the adsorptive. Additionally, the adsorbing solid is called adsorbent. Adsorption is distinguished from absorption, which involves bulk penetration of the gas/vapour into a mass of the adsorbing solid or liquid. [11] [12]

2.1.2 Physisorption and Chemisorption

There are two types of adsorption processes: physical adsorption and chemical adsorption. These are distinguished by the strength and nature of the bond between the adsorbate and adsorbent. [12] In chemisorption, the adsorbate becomes bound to the solid surface by a chemical bond. The energy generated is the same order of magnitude as the heat of reaction,

which ranges between 60 and 4000 kJ/mole [13]. The surface coverage in chemisorption is monolayer. In physisorption, adsorption occurs mainly by van der Waals and electrostatic forces between adsorbate molecules and the adsorbent surface. Because there is no chemical bond between adsorbate molecules and the solid surface, physical adsorption is a reversible process. Physisorption is exothermic and the energy involved is not much larger than the energy of condensation of the adsorbate ranging from 8 to 40 kJ/mole. [13]. It is most likely that adsorption occurs as a monolayer at low pressures and as multilayers at relatively higher pressures, depending on the type of adsorbent and adsorbate used.

2.1.3 Adsorption Isotherms

The quantity of gas taken up by a sample of solid is proportional to the mass *m* of the sample, the temperature *T*, the pressure *p* of the gas and the nature of both the solid and the gas. This can be expressed as *q*, the quantity of gas adsorbed in moles of adsorbate per gram of solid (or grams of adsorbate per gram of adsorbent). A graph reflecting the amount of adsorbed against pressure, or relative pressure, at constant temperature is called the adsorption isotherm.

On an adsorption study, the adsorption equilibrium data is more commonly expressed through adsorption isotherms. For the design of any adsorption process the equilibrium isotherms are one of the more important parameters. The amount of adsorbent needed in the adsorber is determined by the equilibrium data, which in turn determines the key dimension and operation time for the process. [14]

The adsorption isotherm can have different shape depending on the adsorbent-adsorbate interaction. According to IUPAC (International Union of Pure and Applied Chemistry), the adsorption isotherms can be classified into six types. The adsorption isotherms types are shown in Figure 2.1.

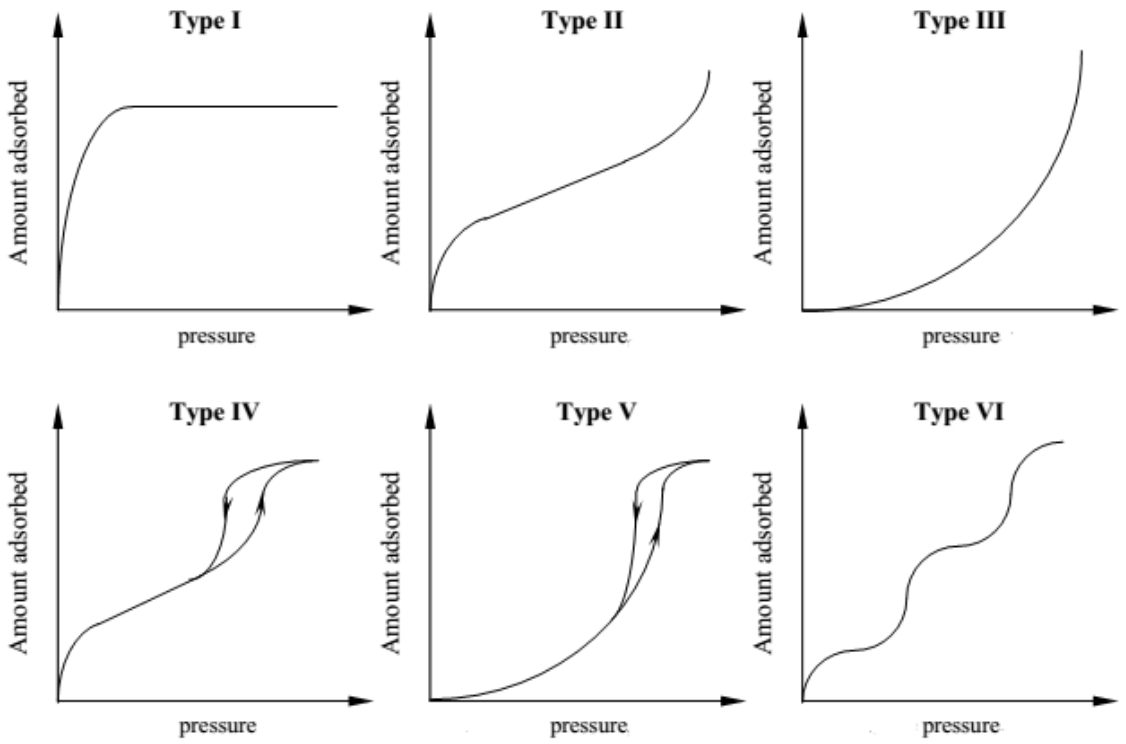


Figure 2.1 – Adsorption isotherms types according to IUPAC (International Union of Pure and Applied Chemistry) [15]

Type I isotherm shows a rapid increase in the amount of gas adsorbed over the low relative pressure range and then reaches a plateau in the high pressure range. Type I isotherms are sometimes referred to as Langmuir isotherms and are often obtained when adsorption is restricted to a monolayer. Type I isotherms have been found for physical adsorption on solids containing very narrow or slit pore structures like activated carbons or metal organic frameworks.

The Type II isotherms are typically produced by solids which are non-porous or macroporous and the isotherms represent unrestricted monolayer-multilayer adsorption on a heterogeneous adsorbent. These are often referred to as the sigmoid isotherm.

Type III isotherms are distinguished from Type II isotherms by a convexity towards the relative pressure axis entire range of the isotherm. At low pressure region, Type III isotherms demonstrate very low uptake of adsorbate due to the forces of adsorption in the first monolayer being relatively small. The adsorbate-adsorbate interactions are stronger than adsorbate-adsorbent interactions.

The Type IV isotherms are found in many mesoporous solids. A characteristic feature is that the adsorption branch of the isotherm is not the same as the desorption branch of the isotherm and hysteresis is observed. Generally, the hysteresis loop occurs due to the capillary condensation taking place in mesopores.

Type V isotherms, unlike Type III, exhibits a point of inflection at a higher relative pressure. Subsequently, the Type V isotherms reach a plateau in the multilayer region of the isotherm where the capillary condensation occurs. Type V isotherms occur most often with mesoporous adsorbents.

The Type VI isotherm represents the step-like nature of the adsorption process. The steps result from sequential multilayer adsorption on a uniform non-porous surface. Each step-height represents the monolayer capacity for each adsorbed layer. [16]

2.2 Adsorption Measurement Techniques

Several adsorption measurements techniques can be used to determine the adsorption properties of an adsorbent-adsorbate system. This includes adsorption equilibrium, kinetics and heat of adsorption data. All these parameters are key variables for modelling and simulation of any adsorption-based separation process. The most commonly available techniques for the measurement of adsorption equilibrium are classified into three types: calorimetric, gravimetric and volumetric methods [17].

Gravimetric and volumetric methods are widely used for the measurement of adsorption isotherms. Both require an accurate estimate of the volume of the solid adsorbent, in the former method, to make a buoyancy correction and, in the later one, to calculate the volume occupied by the gas phase in the sample cell. [17] The calorimetric method is another important technique employed in adsorption studies and can complement gravimetric and volumetric studies.

2.2.1 Calorimetric Method

This type of measurements is less common than volumetric and gravimetric methods.

The calorimetric method measures the temperature variation during the occurrence of adsorption. These measurements are not much less accurate than gravimetric or volumetric methods. Although this method can be useful to study the heat of adsorption, this method is rarely used to determine experimental isotherms [18]. In order to be more effective, this method may be combined with volumetric and/or gravimetric methods.

2.2.2 Gravimetric method

The gravimetric method consists of exposing a clean adsorbent sample to an adsorbate at constant temperature. The change in the weight of the adsorbent sample, pressure and temperature are measured. When those measured quantities no longer vary, the equilibrium is assumed to be reached.

This method allows the direct measurement of the amount adsorbed. The gravimetric method is considered a well-established and accurate technique. With the current equipment available in the group's laboratory, a Rubotherm magnetic suspension balance [19], this method can be much more accurate than the volumetric method, although more time consuming. A gravimetric method apparatus is shown on Figure 2.2.

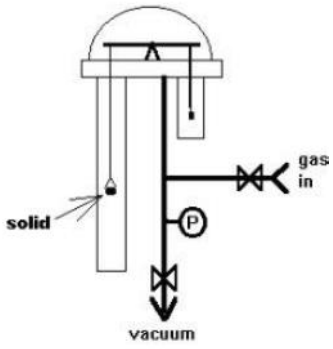


Figure 2.2 – Gravimetric Method Apparatus [20]

The gravimetric adsorption measurements have a diversified use, from characterizing porous media, measuring gas adsorption equilibrium, and investigating adsorption kinetics [21].

2.2.3 Volumetric Method

The oldest method still in use for the measurement of adsorption equilibria is the volumetric method, also known as manometric method. The best term to use is still in debate, since the amount adsorbed is measured by the change in gas pressure while the volume is kept constant [21] [22]. However, during this thesis the term volumetric will the primordial choice.

The measurement of gas adsorption isotherms through the volumetric method, gives an indirect measurement of the amount adsorbed. It consists of feeding gas to a reference cell and, subsequently, expanding it into an evacuated adsorption cell containing a clean adsorbent. This procedure should be ideally performed at constant temperature but, with the heat release due to adsorption,is necessary to wait some time for temperature equilibration [21] [23].

Upon expansion, the sorptive gas is partly adsorbed on the surface of the sorbent material, partly remaining in the gas phase. The amount of gas being adsorbed can be calculated, through a mass balance, if the volume which cannot be penetrated by the sorptive gas molecules is known [14]. An example of the block diagram of a simple volumetric unit setup is shown in Figure 2.3.

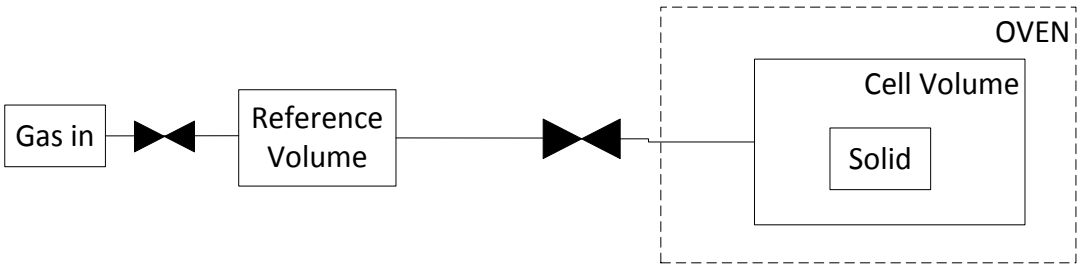


Figure 2.3– Volumetric Method scheme

In order to obtain an isotherm, the method mentioned above needs to be performed for the same number of times as the amount of experimental points desired. After the first expansion and following pressure equilibrium, the data obtained only origins one single point in the isotherm measured.

Alternatively, to start each measurement point from vacuum, the following points may be measured taking into account the amount of gas that remains in the adsorption chamber from

the previous point. Successive measurements lead to the final data necessary to determine an isotherm.

2.2.3.1 Pros and Cons of Volumetric Method

Advantages

The volumetric gas adsorption instruments are simple and do not require any sophisticated high-tech equipment. Furthermore, the experimental procedure is also simple. For that reason volumetric instruments can be automated and run without permanent supervision.

Volumetric measurements of gas adsorption equilibria are reduced to the measurement of the gas phase pressure and temperature. A great variety of high sensitivity instruments for pressure and temperature measurement are nowadays available, allowing operating in diverse ranges and even in corrosive environments [21].

In the volumetric method, the adsorption cell can be easily inside an oven, which allows the activation of the adsorbent in-situ. In contrast, the gravimetric balance usually does not support higher activation temperatures, thus limiting the solid activation or regeneration inside the adsorption gravimetric cell.

Disadvantages

The amount of sorbent material necessary for volumetric experiments is higher than the sample needed for the gravimetric method. For volumetric measurements usually several grams of adsorbent material are needed.

In gas expansion and adsorption processes with remnant gas in the adsorption chamber, the experimental error in the determination of the adsorbed mass increases with each step performed. This fact limits the number of points that can be measured with a satisfactory experimental error [21].

2.3 Adsorbates chosen

2.3.1 Carbon Dioxide

Carbon dioxide (CO_2) is a naturally occurring chemical compound composed of 2 oxygen atoms each covalently double bonded to a single carbon atom.

The environmental effects of carbon dioxide are of significant interest. A great amount of the CO_2 released into the atmosphere results from the burning of fossil fuels, mainly by the energy production, industry and transportation sectors [24]. The amounts released since the industrial revolution led to global warming due to the CO_2 greenhouse gas properties [24].

2.3.2 Nitrogen

Nitrogen (N_2) is a colourless and odourless gas of diatomic molecules and it forms about 78% of Earth's atmosphere.

It is also important to study the adsorption equilibrium of N_2 in order to better understand and allow the modelling and design of adsorption-based processes for the separation of CO_2/N_2 which are the main components present in flue gases from fossil fuelled power stations [25].

2.4 Adsorbents

The International Union of Pure and Applied Chemistry (IUPAC) has defined a porous material (or porous solid) as a solid with pores i.e. cavities, channels or interstices, which are deeper than they are wide [12] [26].

According to IUPAC, pores are generally classified into three categories, namely:

- Micropores, which have diameters smaller than 2 nm (<20 Å). These are sometimes called nanopores;

- Mesopores, which have diameters between 2 and 50 nm(20-500 Å);
- Macropores, which have diameters larger than 50 nm (>500 Å);

Porous materials demonstrate scientific and technological interest because of their ability to interact with atoms, ions and molecules not only at their surfaces, but also in bulk. The pore sizes, shapes and volumes govern the adsorbent ability for performing the desired function in any particular application. The most important attributes of an adsorbent for any applications are its capacity, selectivity, regenerability, kinetics, compatibility and cost. [27]

Adsorption capacity is the most important characteristic of an adsorbent. Adsorption capacity is of paramount importance to the capital cost a separation process, because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels. Selectivity is related to capacity, and is the ratio of the capacity of one component to that of another at a given fluid concentration. That ratio generally approaches a constant value as concentration decreases towards zero.

All cyclic adsorption applications rely on regenerability, so that the adsorbent can operate in sequential cycles with uniform performance. This mean each adsorbable component must be relatively weakly adsorbed to allow a regeneration step with moderate energy consumption.

The most common commercial adsorbents include silica gel, activated alumina, activated carbon, carbon molecular sieves and zeolites. Lately, metal-organic frameworks (MOFs) have arisen as an interesting adsorbent material and, therefore, a huge amount of studies have been recently published about MOFs. [28] [29] [24]

2.4.1 Activated Carbon

European Council of Chemical Manufacturers' Federation defined activated carbon as non-hazardous, processed, carbonaceous products which have a porous structure and large internal surface [30].

Activated carbons are used since the Ancient Egyptians utilized its adsorbent properties for purifying oils and for medicinal purposes. Many centuries later, during the First World War the activated carbons proprieties were used to develop appropriate masks for personnel protection. During the Second World War activated carbon properties were used for the entrapment of nerve gases. Since then the activated carbons were continuously studied in order to use them for separation and storage of gases [2] [31].

Activated carbon is a generic name for a group of porous carbon materials produced by carbonization of carbon-rich organic precursors, followed by physical or chemical activation. These activation processes produce a high porosity and surface area which is suitable for removal of impurities from gases and liquid, gas storage and separation processes [32] [33].

Activated carbons adsorb species from both gaseous and liquid phases and the adsorption process is influenced by the pore size distribution of the activated carbon and size, structure and properties of adsorbate. The usage of carbon adsorbents depends on their surface area, pore size distribution and surface chemical characteristics.

Activated carbons are the most widely used adsorbents. Activated carbons are microporous adsorbents that can be obtained from several raw materials. Basically, the materials that show a high fixed carbon content are potentially able to be activated. The properties of activated carbons are directly related to the nature of the starting material, the type of production method and the temperature of production. In Figure 2.4 a representation of an activated carbon porous matrix is showed.

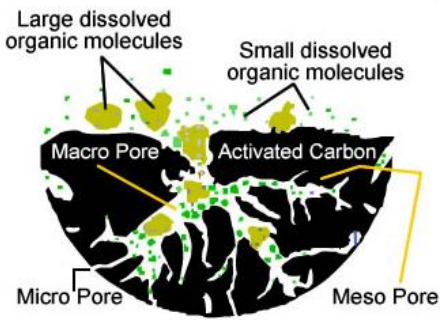


Figure 2.4- Representation of an activated carbon porous matrix [34]

The materials are converted to activated carbon by a process of manufacture involving the following steps: preparation of the material, pelletization (if that is the case), carbonization at low temperature (400-500°C) to remove volatile materials, and activation that consists on a partial oxidation (800-1000°C). The activation process creates a porous structure in the carbon, whose surface area can range from a few square meters per unit mass or exceed 2000 m^2 / g. If the preparation conditions are carefully controlled, one can achieve the desired pore structure with good mechanical strength and resistance to attrition.

In continuous adsorption separation processes, extruded activated carbons are preferably used because they offer a lower pressure drop, due to its regular shape.

These unique pore structures play an important role in many liquid and gas phase applications because of their adsorptive capacity. Activated carbon can be used as a catalyst, decolourant or filter, on environmental or medical field and also for gas storage [1]. One of the main applications, gas storage is characterized by storage at low pressure and low volume. This improves the safety criteria and reduces the costs when compared with the traditional storage methods.

2.4.2 Metal Organic Framework (MOF)

A metal-organic framework (MOF) is composed of two major components: a metal ion, or cluster of metal ions, and an organic molecule called linker. The organic units are typically mono, di-, tri-, or tetravalent ligands. The combination of the metal ion or cluster and the organic linker provides endless possibilities for the development of MOF structures [35]. Furthermore, pore size of these frameworks can be expanded or collapsed [36] [37] [38].

The MOFs have been explored due to their interesting optical, magnetic, and electronic properties, as well as their potential applications such as in catalysis, ion-exchange, gas storage and separation, sensing, polymerization and drug-delivery [35].

MOFs attracted attention as materials for adsorptive gas separation and storage because of their exceptionally high specific surface areas and chemically tunable structures. MOFs can be considered as a three-dimensional grid. Gas molecules are stored in a MOF by adsorbing to its surface without space-blocking by non-accessible volume. Also, MOFs have a fully reversible uptake-and-release behaviour: since the storage mechanism is based primarily on physisorption, there are no large activation barriers to be overcome when liberating the adsorbed gases [39].

The MIL-n (Materials of the Institute of Lavoisier) MOF series, were synthesized by Férey and co-workers. MIL materials are accepted as promising candidates for the adsorption of some important gases, such as CO_2 [40] [41].

The MIL-53(Al), or Aluminium Terephthalate, is a hydrophilic metal-organic framework (MOF) that can be used for adsorption applications. This is a very interesting class of MOFs because they not only adsorb large quantities of gas, but also presents an exceptional flexibility undergoing a reversible structural transformation between two distinct conformations - large pore (lp) and narrow pore (np). Both conformations share the same chemical composition. At room temperature and in the absence of the adsorbate molecules, the lp phase is the most stable

form. However, during gas adsorption, the lp phase becomes np at low pressures and inverse transformation occurs at higher pressures [29] [28] [41]. Figure 2.5 shows a representation of MIL-53(Al).

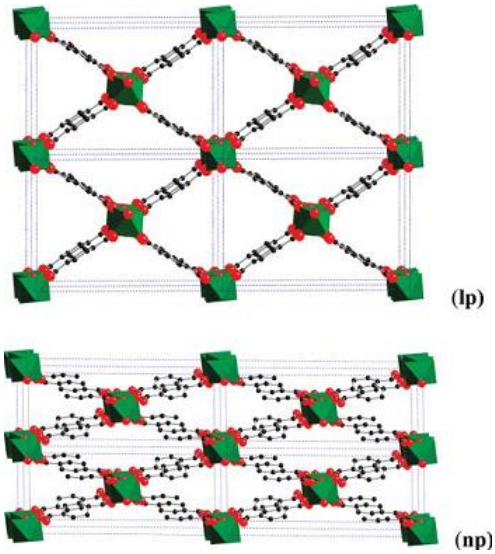


Figure 2.5- Representation of the metastable lp and np structures of the MIL-53(Al) material, as a 2 ×2×2 supercell viewed along the axis of the unidimensional channels [28]

3. CONSTRUCTION AND ASSEMBLY OF THE VOLUMETRIC UNIT

The main objective of this thesis was the design, construction, assembly and validation of a volumetric adsorption unit for measurement of equilibrium data.

This chapter covers the description of the volumetric adsorption unit and the software developed for unit control and data acquisition. The volumetric unit can be divided in two parts: the main section and section which includes the electrical supply, data acquisition and control. The unit development comprised the design, and then the selection of the necessary material in order to do a proper assembly. After this, the unit was build-up and then proper software was developed to control the volumetric unit and acquire the data obtained.

3.1. Volumetric Unit Design

The volumetric unit was designed with the possibility of employing a maximum of two adsorption cells, i.e., two adsorbent samples can be tested at the same time. It would be possible to design a unit for the test of more samples in parallel, but this would greatly increase the complexity of the apparatus and also its cost. Nonetheless, future work may include the build-up of more gas lines and adsorption cells to allow gathering more data at the same time. The scheme of the designed volumetric unit is shown in Figure 3.1 and a detailed description of the equipment employed is provided in Table 3.1.

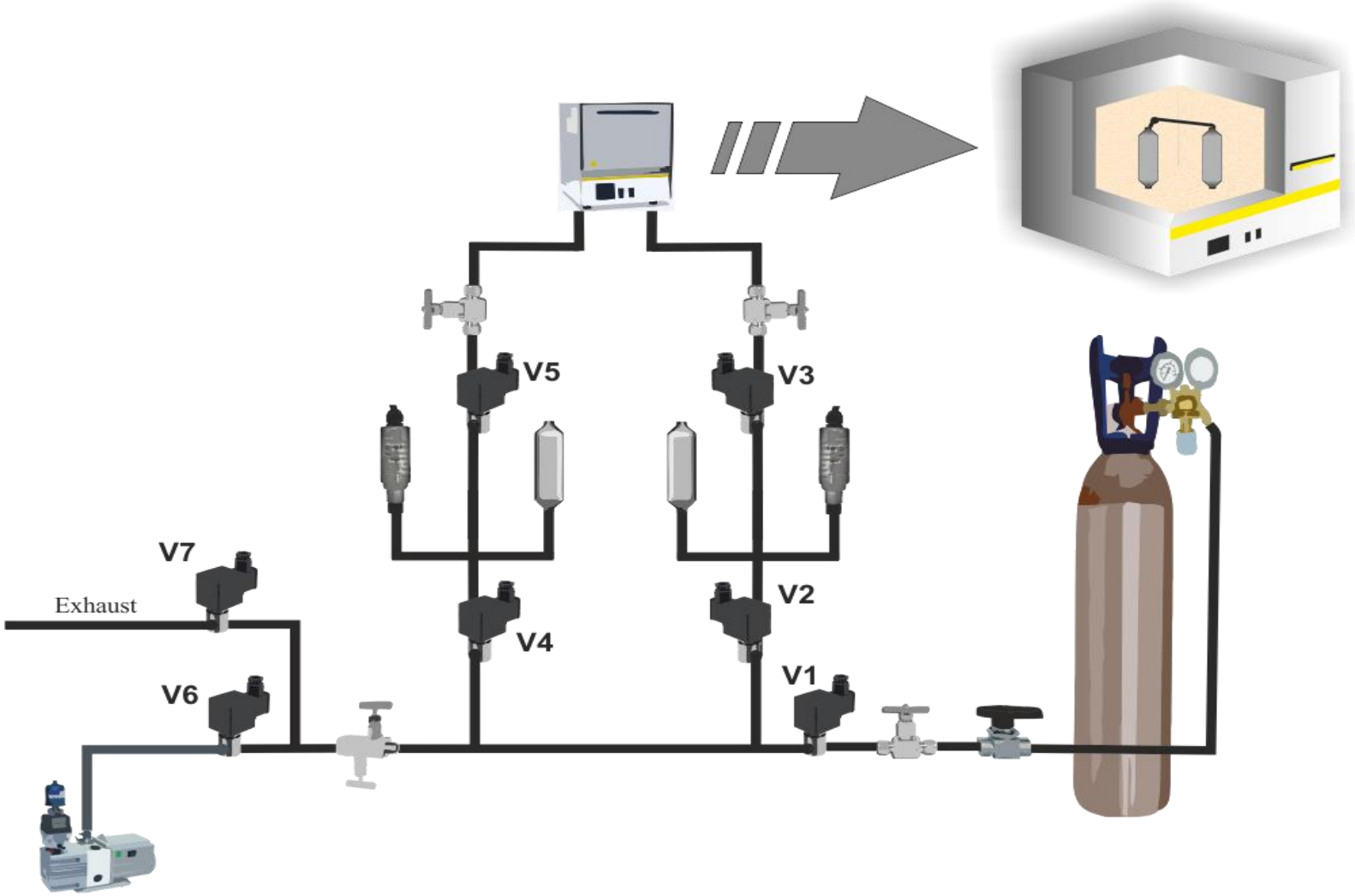


Figure 3.1– Schematic Representation of the Volumetric Unit Apparatus Built

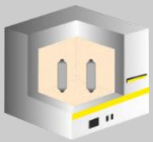
Equipment shown on Figure 3.1	
	Gas cylinder containing the pure gases employed in the experiments performed using the volumetric unit. CO_2 and N_2 were used to perform the several tests. Helium was used for calibration purposes
	Needle valves. The main objective is to control the gas flow during pressure increase and decrease steps
	Solenoid valves. Function in opened or closed position, controlling the gas passage. They are controlled by a LabVIEW interface
	Double needle valve. Its objective is to control the gas flow. Each one of the heads leads to different flow control. This valve allows a more sensitive control than the simple needle valves.
	Ball valve. Opens or closes the gas path between the gas supply and the volumetric unit
	Calibrated volume cylinder. Used to be filled in with gas before the expansion to the adsorption cell
	Pressure sensor. Measures the pressure data *in situ* and send an acquisition board managed by LabVIEW
	Oven. Ensures constant temperature of the adsorption cells during the experiments.
	Adsorption cells. It is where the adsorbent materials under study are placed, and where adsorption occurs.
	Vacuum Pump. Provides vacuum for adsorbent activation and adsorption equilibrium experiments

Table 3.1 – Equipment of the Volumetric Unit

3.1.1 Material

After the unit design, it was required to select the necessary material and equipment in order to build-up the volumetric unit. On table 3.2, the materials used are described in more detail and the cost of each piece is showed. The approximate cost of this unit was 9080€.

Equipment	Reference	Company	Country	Price/€
Oven	Tmax=1100ºC; 50/60Hz; 13.0A;3.0kW	Nabertherm	Germany	3249,95
1Acquisition / Control Board	USB-6008 12-bit, 10kS/s Multifunction I/O and NI-DAQmx Software	National Instruments Corp	USA	204,98
1 Relay Board	USB-OPTO-RLY88 I/O USB Module	Robot-Electronics	UK	75,50
1 Power Supply	AC-DC; 24V@1.3A; 85-264VIn; Enclosed; DIN Rail Mount; SITOP Power Series	Siemens	Germany	41,65
Tubing, fittings	316 Stainless Steel, ¼ and ⅛ inches	Swagelok Company	USA	1000,00
7 Solenoid valves	2/2 NF 1,2 mm NF ⅛ NPT inox body NBR	Asco Numatics	USA	815,74
4 Needle valves	316 Stainless Steel, 1/16 inches	Swagelok Company	USA	568,00
2 Pressure Transducer	Pressure TX, High Acc 0.05%, 0-300PSIA, OUT 0-5VDC, 1/4-18NPT-F, Twist Lock Conn	Omega	UK	1423,08
2 PT-100 probes	conex. PTFE,100mm	RS Amidata	Portugal	86,80
2 Sample Cylinders	316 Stainless Steel, 40 c.c.	Swagelok Company	USA	153,00
1 Vacuum Pump	RV3 115/230V, 1-ph, 50/60Hz	Edwards	UK	1548,00

Table 3.2 - Material used for the build-up of the volumetric unit

Following the selection of the equipment and its acquisition, the unit was built. In Figure 3.2 the volumetric unit developed is displayed.

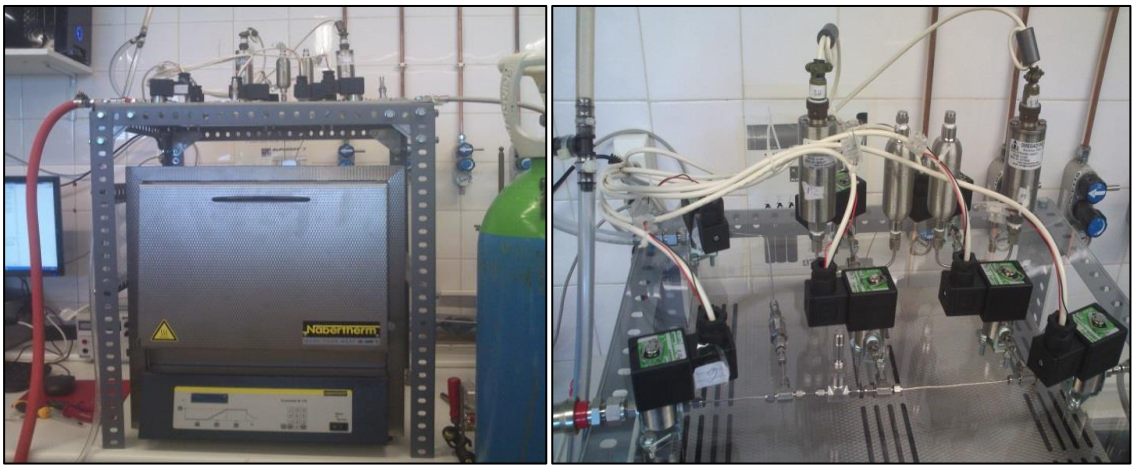


Figure 3.2– General View of the Volumetric Unit

3.1.2 Main Section

The main section comprises the area where the adsorption process will take place. Excluding the gas supply, the electrical section and the vacuum pump, all the remaining material is included in this section.

3.1.2.1 Section above the oven

Pressure transducers are essential to collect the necessary pressure data. The two pressure transducers (Omega Eng, UK) have a range of 0-20 bar and are connected directly to the USB data acquisition board. They have an error of 0.01 bar. The solenoid valves (Asco Numatics, USA) are connected to the relays board and are responsible for opening and closing the gas path along the tubing. The valves have only two functions, the on (opened) and off (closed) functions. Four are used to establish the reference volume (two for each line), the space between valves V2 and V3 for line 1 and V4 and V5 for line 2. Also three more valves are used to manage the gas feed and discharge, one for the gas entry and two at the gas exit (one for the vacuum line and the other for the atmospheric

line). Their position is shown on Figure 3.1. The needle valves (Swagelok, USA) are used to control the gas flow. There were used four needle valves, one before the first solenoid valve, V1, and after the gas entry, one on each line after the correspondent solenoid valve that ends the reference volume and one before the vacuum and atmospheric lines. The sample volumes (50, cm^3, Swagelok, USA) are used to obtain a certain reference volume. The PT-100 (RS Amidata, Spain) probes are used to acquire temperature data. The tubing used is stainless steel with $^1/_8$ inches of diameter on the reference volume, and the rest of the unit uses tube with $^1/_{16}$ inches of diameter. Both tubes were supplied by Swagelok, USA. Figure 3.3 shows a detail of the main section.

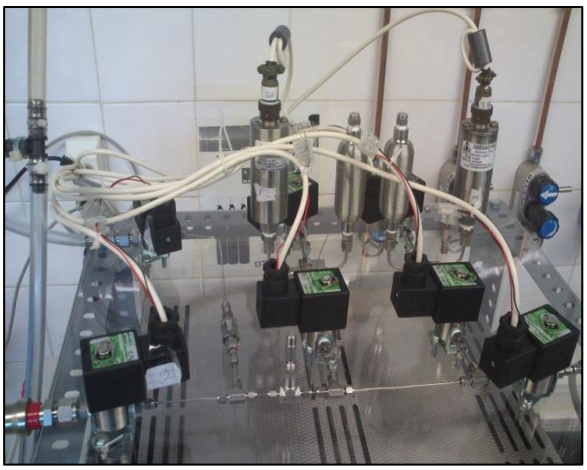


Figure 3.3 - Detail of the Volumetric Unit Main Section

3.1.2.2 The oven

The oven (Nabertherm, Germany) is an electronic temperature controller with integrated excess temperature protection with a temperature range between 0-1100ºC. Inside the oven, only the two sample cells and the corresponding stainless steel tubing are present, as shown on Figure 3.4.

Figure 3.4 - Detail of the two adsorption cells inside the Oven

3.1.3 Electrical and Data Acquisition/Control Section

On the side of the unit was built the section of electrical supply and data acquisition and control. It consists of a 24V DC power supply (Siemens, Germany), a relay board with USB connection (Robot Electronics, UK) and a USB data acquisition board (National Instruments, USA). The relay board has 8 relay output, but in this case, only seven are used (one for each valve). Each one of these signals is connected to a specific valve and is LabVIEW commanded by communication through an USB port. The data acquisition board (National Instruments, USA) is connected to the PC by a USB port, which serves for communication and also power supply. The 24V DC power supply (Siemens, Germany) provides power for the pressure transducers. This section is shown in Figure 3.5.

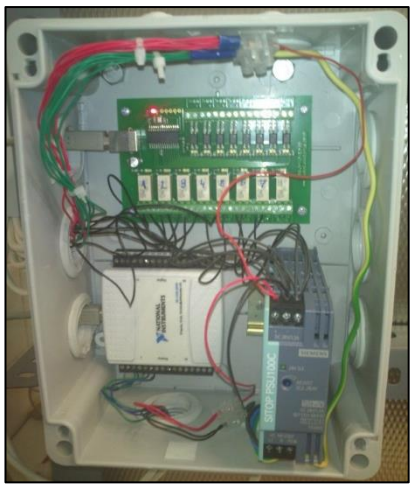


Figure 3.5 – Electrical and Data Acquisition/Control Section

3.1.4 Complementary Sections

The Complementary section comprises the remaining material used that does not belong in the previous sections. The gas supply is given to the unit using a cylinders acquired from Air Liquide. The purities of the gases employed are: CO2 > 99.998%, N2 > 99.995%, and He > 99.999%. The vacuum pump was acquired from Edwards, United Kingdom and provides vacuum for adsorbent activation and adsorption equilibrium experiments.

3.2. Control and Acquisition Software

For the control and data acquisition of the volumetric unit the software LabView was used.

LabVIEW (Laboratory Virtual Instrument Engineering Workbench) is a graphical programming language first released by National Instruments in 1986. This software uses icons instead of lines of text to create applications. In contrast to text-based programming languages, where instructions determine program execution, LabVIEW uses dataflow programming, where the flow of data determines execution. Its graphical nature makes it ideal for test and measurement, automation, instrument control, data acquisition, and data analysis applications. This results in significant productivity improvements over conventional programming languages.

The LabVIEW programming element is called a Virtual Instrument (VI). A VI consists of a front panel, block diagram, and an icon that represents the program. The front panel is used to display controls and indicators for the user, while the block diagram contains the code for the VI. The icon, which is a visual representation of the VI, has connectors for program inputs and outputs.

Similar to most programming languages, LabVIEW supports all common data types such as integers, floats, strings, and clusters (structures) and can readily interface with external libraries, ActiveX components, and .NET framework. Applications may be compiled as executables or as Dynamic Link Libraries (DLLs) that execute using a run-time engine similar to the Java Runtime Environment.

3.2.1 The front panel

When a blank VI is opened, an untitled front panel window appears. This window displays the front panel and is one of the two LabVIEW windows used to build a VI. The front panel is the window through which the user interacts with the program. The input data to the executing program is fed through the front panel and the output can also be viewed on the front panel, thus making it indispensable. [42]

3.2.2 The block diagram

The block diagram window holds the graphical source code of a LabVIEW's block diagram and corresponds to the lines of text found in a more conventional language like C or BASIC –it is the actual executable code. The block diagram can be constructed with the basic blocks such as: terminals, nodes, and wires. After the front panel is built, the user can add code using graphical representations of functions to control the front panel objects. The block diagram contains this graphical source code. Front panel objects appear as terminals, on the block diagram. Block diagram objects include terminals, subVIs, functions, constants, structures, and wires, which transfer data among other block diagram objects. [42] [43]

The Figure 3.6 shows the interface used to control the volumetric unit.

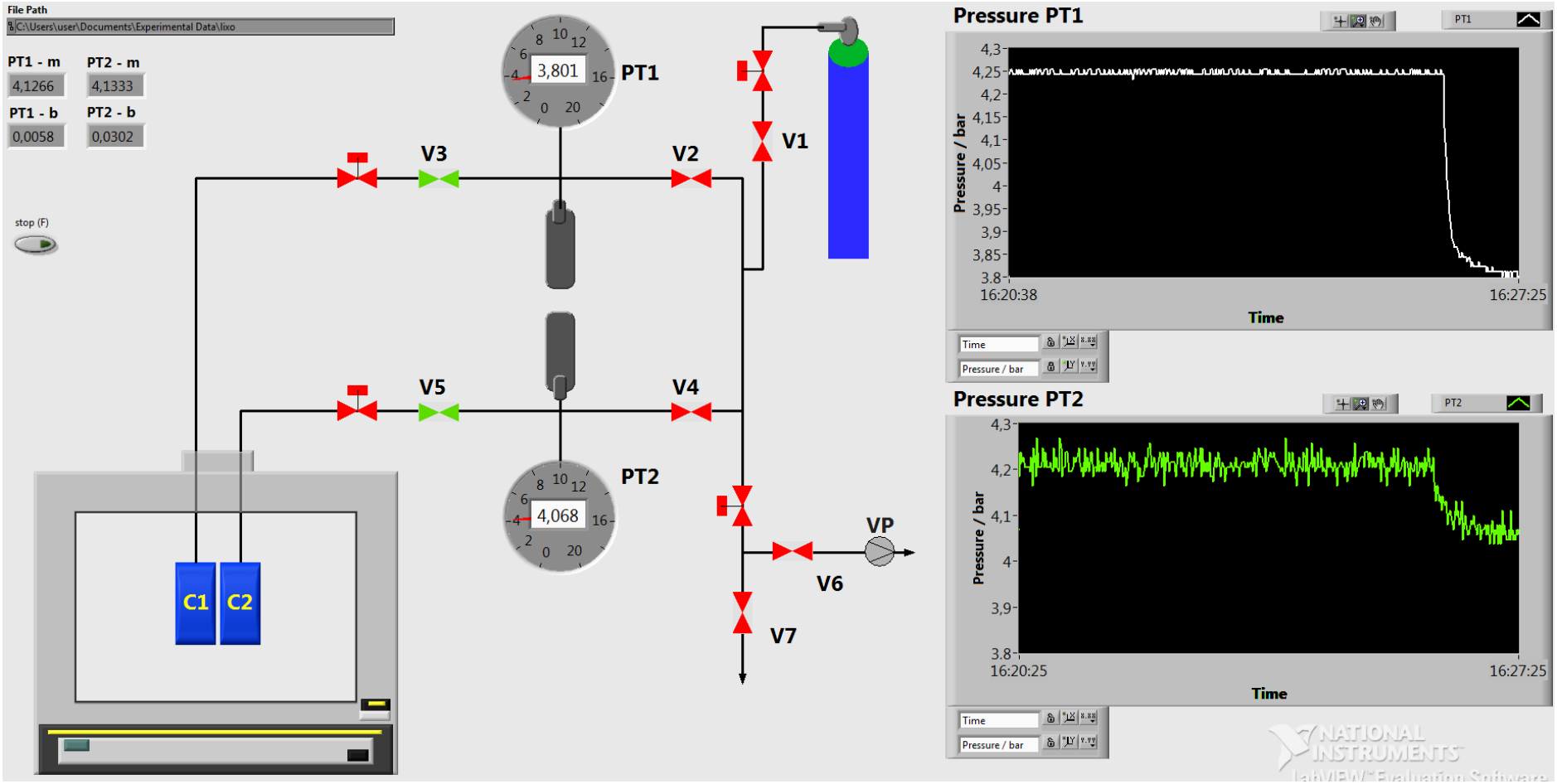


Figure 3.6– Volumetric Unit Interface

The interface shows a scheme of the unit designed with two graphics showing the data read by the each pressure sensor in real time. The valves V1 to V7 represent the solenoid valves and control the valve position (opened/closed) by clicking with the mouse above the represented controller. This is the only controller in the interface. All the other pieces are only representations or indicator (in the case of the pressure sensor, which provides the reading of the pressure at each second. The oven, the gas bottle and the needle valves are manually controlled. The file path represented on the interface is used to choose the PC location to store the data read from the pressure sensors.

This interface was constructed by manipulating the block diagram on LabView.

The first step is to create the valve control. The valves shown on the interface are controllers that send the information to the relays board which then send the same information the solenoid valves. The open/close function is observed by the green/red colour change on the valves shown in the interface.

After the valve control, acquisition of the data obtained by the pressure sensors was programmed. It was used the DAQ assistant on the block diagram, which allows the data collection by configuring and calibrating each sensor. Figure 3.8 shows the LabVIEW DAQ assistant on the block diagram.

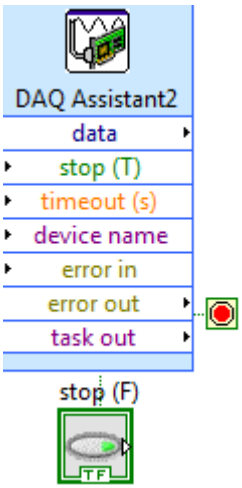


Figure 3.7 – LabVIEW DAQ assistant

Finally, it was used the “write to file” function in order to secure the data (time and pressure) in an independent file, that can be read, for example, with Notepad. Then the data is transferred to a Microsoft Excel file for further analysis.

3.3 Initial Measurements

After the assembly of the unit and the conclusion of the LabView interface the apparatus was ready to be tested. At this stage, the first task to perform was the calibration of the reference and cell volumes. The rigorous knowledge of these values is fundamental to solve the mass balances that will allow the determination of the adsorbed amounts.

3.3.1. Reference Volume Calibration

The determination of the exact values (calibration) of the reference and cell volumes was performed using a vessel (or cylinder) with known volume. The calibration procedure was the same for both lines so only one of them is described.

Firstly is necessary to add a new cylinder with a known volume in order to determine the amount of gas added to the unit. The Figure 3.8 shows this auxiliary vessel connected to the gas feed line.

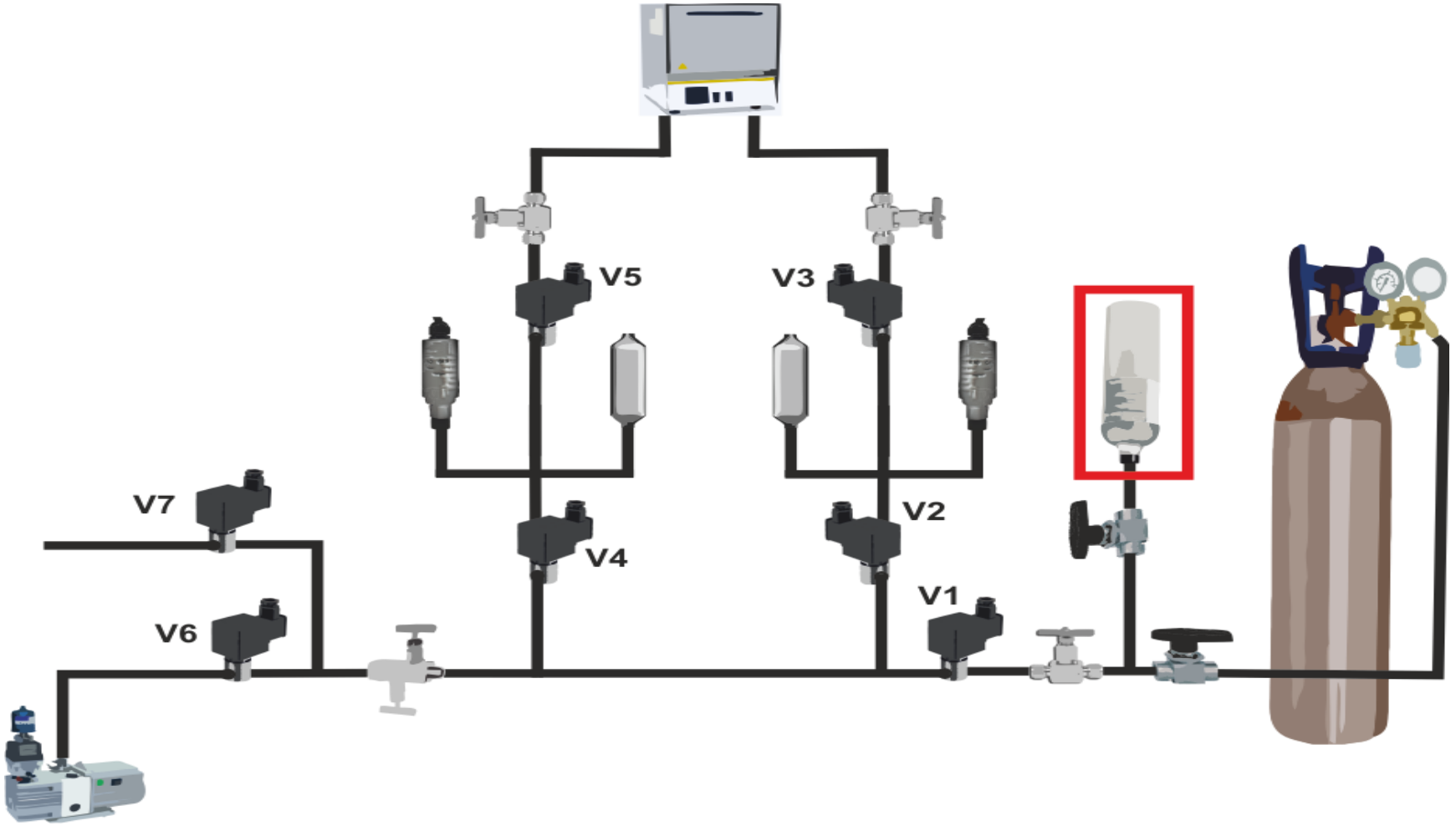


Figure 3.8– Volumetric Unit apparatus with the auxiliary vessel

Initially all parts of the unit must remain under vacuum. Then the valve closing the auxiliary cylinder is opened along with valves V1 and V4 and a certain amount of pressure is fed to the opened parts of the unit. This is represented in Figure 3.10. The pressure is measured with the sensor on the green line.

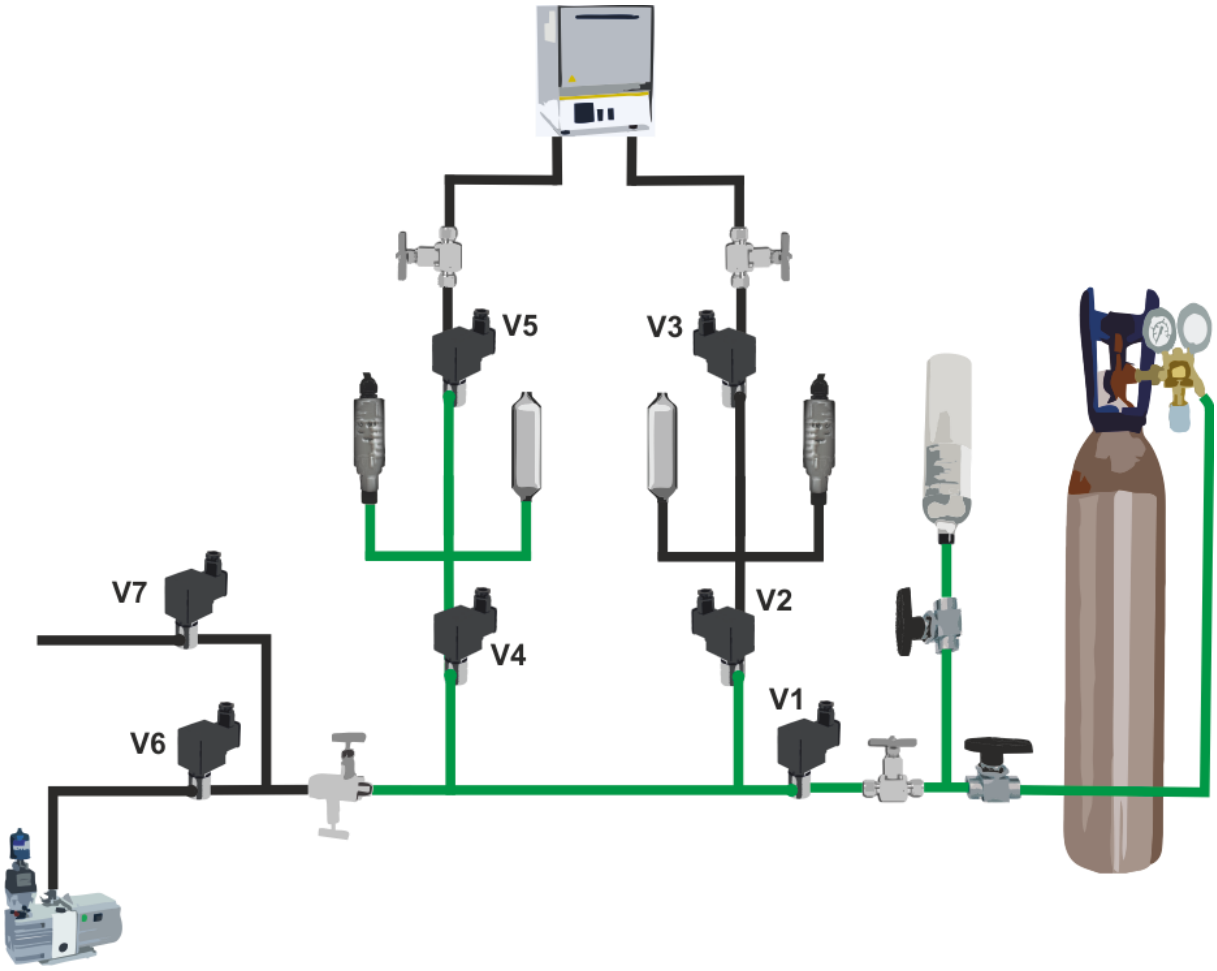


Figure 3.9 - First step for volume calibration procedure

After this, the vessel of known volume is closed containing a known amount of gas (pressure and temperature conditions were measured prior to closing the cylinder). The next step is to repeat the vacuum condition but with the auxiliary cylinder closed. This allows the use of the gas stored in the cylinder to determine other volumes by gas expansion with pressure measurement. The auxiliary cylinder is then opened along with the valves V1 and V4. With this step the volume that comprehends the green line represented in Figure 3.10 can be calculated. This volume will be called residual volume (V_{res}).

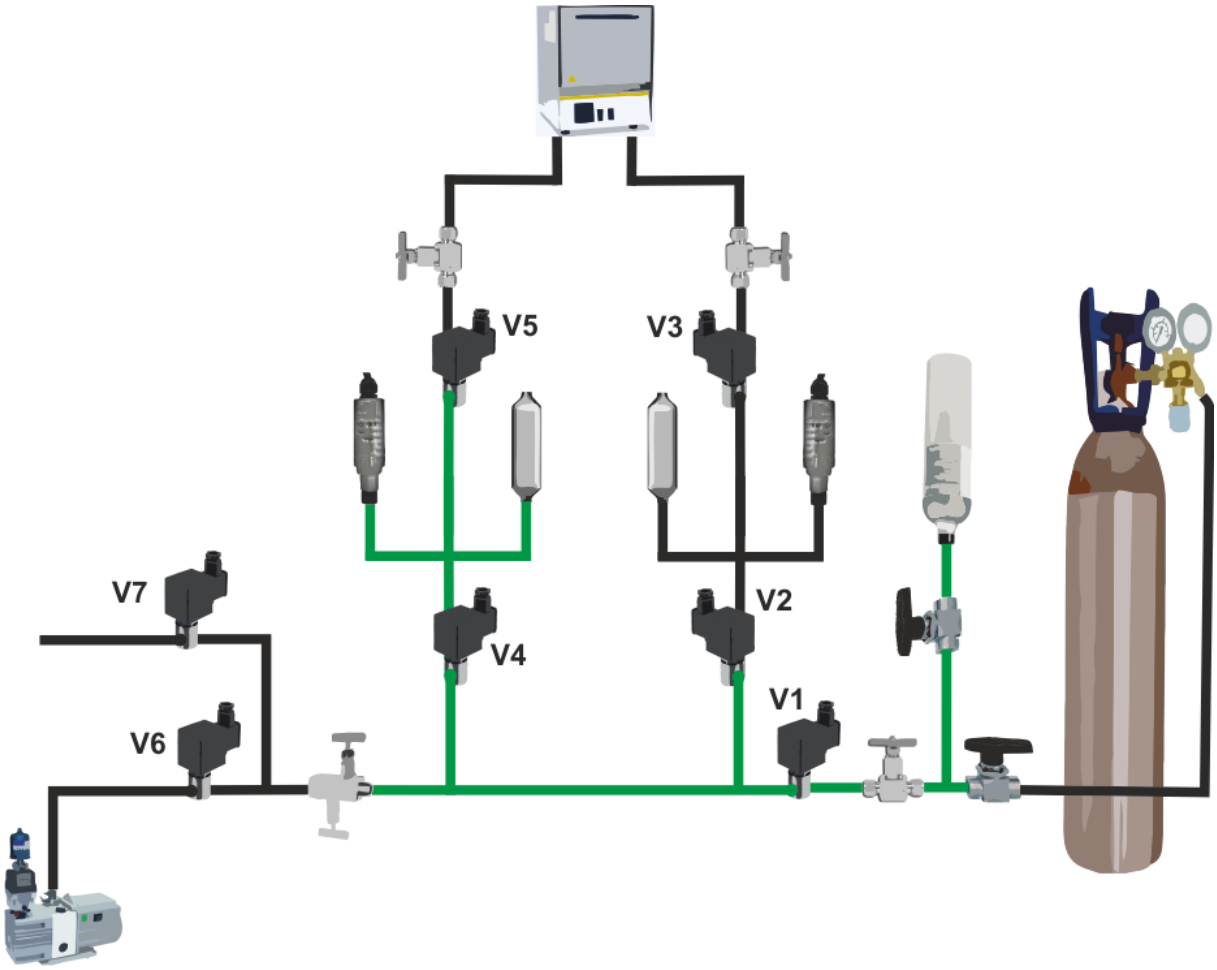


Figure 3.10 - Second step for volume calibration procedure

Then V2 is opened, as show on Figure 3.11. This several steps will allow determining an important volume in each line: the reference volume. For the case of line 1, the reference volume is placed between the valves V2 and V3. The same procedure was employed for determination of the reference volume in line 2.

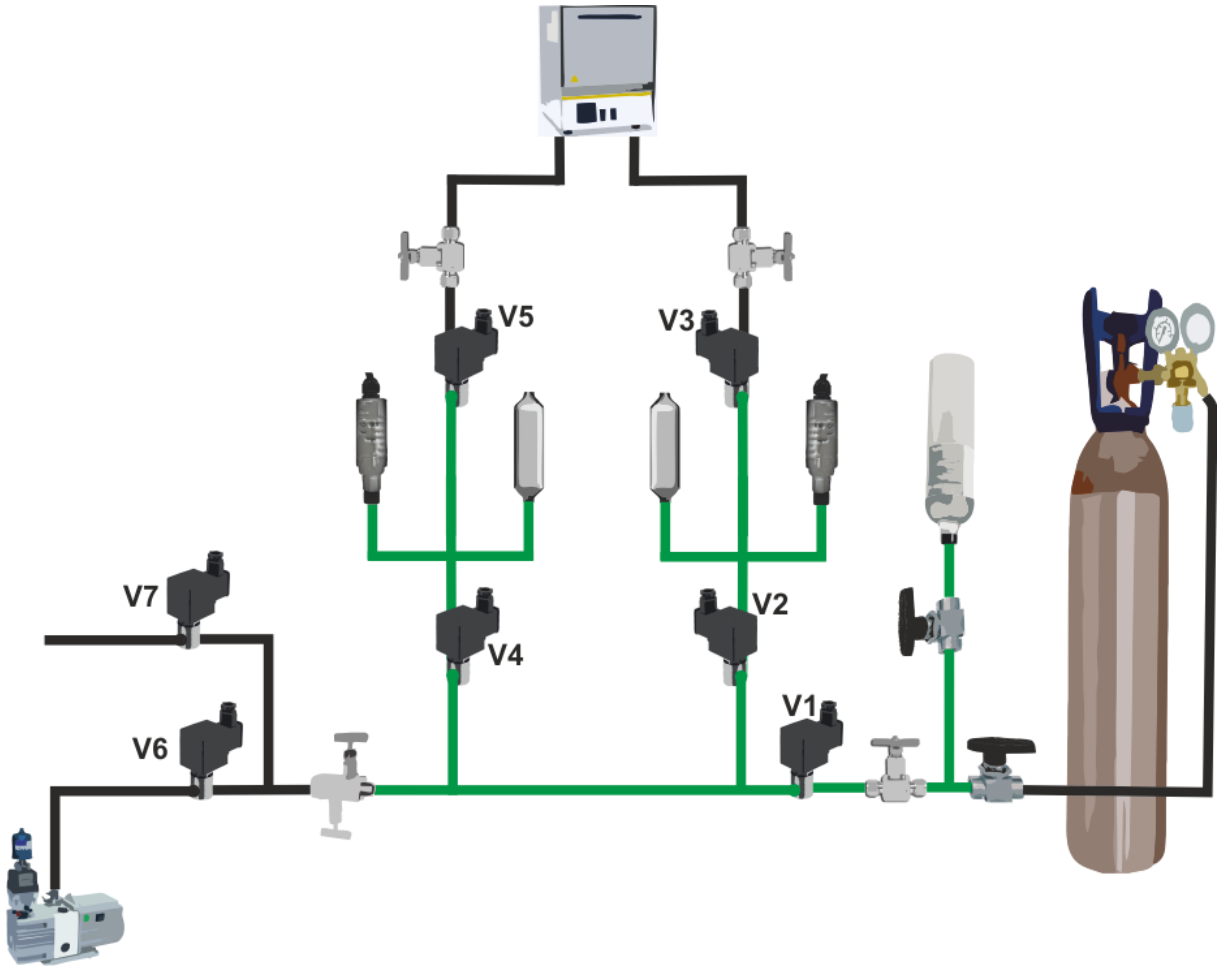


Figure 3.11 - Final step for volume calibration procedure

The volume calculations on the second step, the residual volume, were performed employing the ideal gas law (equation 1).

$$PV = nRT$$

Equation 1

Since the amount of gas present in the system is maintained, the mass balance of equation 2 can be used.

$$\frac{P_{cyllinder} V_{cyllinder}}{T_{cyllinder}} = \frac{P_{Res} V_{Res}}{T_{Res}}$$

Equation 2

Regarding that the apparatus is all at the same temperature, equation 2 can be simplified to

$$P_{cyllinder}V_{cyllinder} = P_{Res}V_{Res} \Leftrightarrow V_{Res} = V_{cyllinder}\frac{P_{cyllinder}}{P_{Res}}$$

Equation 3

Where V_{Res} is the volume for the first step on the calibration process. In order to obtain the reference volume similar equations can be used. Assuming that the temperature is the same,

$$P_{cyllinder}V_{cyllinder} = P_{T}V_{T} \Leftrightarrow V_{T} = V_{cyllinder}\frac{P_{cyllinder}}{P_{T}}$$

Equation 4

Since the objective of this procedure was the determination of the reference volume, a final calculation must be done. The total volume obtained in the previous equation comprehends all the volume show in Figure 3.11. The reference volume is obtained by the difference between this total volume and the volume obtained in the previous step.

$$V_{ref} = V_{T} - V_{res}$$

Equation 5

The same method is used to determine the volumes on the other line.

3.3.2 Cell Volume Calibration

The procedure for determination of the cell volume was performed after knowing the value of the reference volumes for each line. This way, the reference volumes were supplied with a known amount of gas (Helium) and, then this gas was expanded to the adsorption cell. This procedure allowed the

determination of the cell volume. For the calculation of the cell volume, the ideal gas law was used and the following equation was obtained. The remaining calculations are on Annex A.

$$V_c = V_{ref} \frac{\left(\frac{P_{r,i}}{T_{ref}} - \frac{P_f}{T_f}\right)}{\left(\frac{P_f}{T_f} - \frac{P_{c,i}}{T_{c,i}}\right)}$$

Equation 6

Where V_c is the cell Volume (Line 1 or 2), P_f the pressure after gas expansion, $P_{r,i}$ is the pressure of the reference volume before expansion, $P_{c,i}$ is the pressure of the cell volume before expansion, T_f the temperature of the system after expansion, T_{ref} is the temperature of reference volume before expansion and $T_{c,i}$ is the temperature of cell volume before expansion.

3.3.3 Final Considerations

After successfully performing the volumes determination, the obtained values for the reference and cell volumes of both lines are represented in Table 3.3.

The obtained volumes characterize the volumetric unit built and will be important to solve the mass balances needed for determination of the amount adsorbed.

Variable	Value	
	Line 1	Line 2
Reference Volume (Vref)	43,433±0,18 cm^3	43,371±0,19 cm^3
Cell Volume (Vc)	2,226±0,48 cm^3	2,551±0,51 cm^3

Table 3.3 – Reference and Cell Volume determined

4. VOLUMETRIC UNIT VALIDATION

In this chapter adsorption studies using both adsorption cells in parallel are presented. For this purpose, an activated carbon, and a MOF were packed inside each cell. Measurement of CO_2 and N_2 adsorption isotherms at different temperatures (30ºC. 80ºC and 150ºC) for carbon dioxide and 50ºC for nitrogen) were performed. The carbon dioxide isotherms data was acquired for a pressure range between 0 and 10 bar for 30ºC and between 0 and 15 bar for 80ºC and 150ºC. The nitrogen isotherms data was acquired for a pressure range between 0 and 20 bar. Later, the results obtained were compared with data obtained by the group in a gravimetric apparatus.

4.1 Adsorbent Activation

The adsorbents selected to perform the volumetric unit tests were materials previously studied by the group. This ensures that the behaviour of the adsorbents to test is already known which facilitates the validation of the unit built. For this purpose an activated carbon (ANGUARD 5 from Sutcliffe Speakman Ltd., UK) in the form of extrudates and a MOF (MIL-53(Al) from BASF SE) in the form of powder were employed. Samples of 0,29 grams of ANG5 and 0,33 grams of MIL-53(Al) were packed in each adsorption cell. Table 4.1 summarizes the properties of the adsorbents employed.

Prior to the measurement of the adsorption equilibrium data, the adsorbents were degassed (or activated). This procedure was performed to remove any impurities and moisture adsorbed in the solids. The activation was performed *in situ*, which is one of the advantages of this newly built apparatus. The procedure consisted in heating the adsorbent samples up to 100ºC (activated carbon) and 200ºC (MIL-53(Al), under vacuum. The heating was performed at a maximum rate of 2ºC/min and after reaching the temperature defined this temperature was kept constant for at least four hours.

	ANGUARD 5 [19]	MIL-53(Al) [29]
BET surface area (m^2/g)	1342	831
Total pore volume (cm^3/g)	0,881	0,597
Micropore volume (cm^3/g)	0,777	0,332

Table 4.1 - Properties of the adsorbents employed

4.2 Adsorption Equilibrium Measurements

First it is imperative to determine the equations that will be used for the determination of each isotherm.

The primordial equation to be used in every calculation is the real gas law. The following image illustrates what happens during the volume expansion.

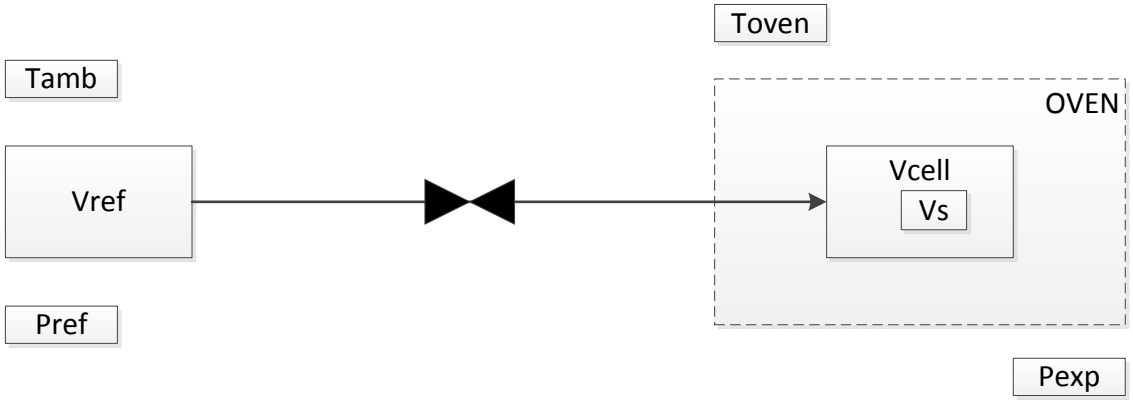


Figure 4.1 - Volume Expansion illustration

In the first step, the gas is at room temperature with initial pressure of P_{ref} (pressure at reference volume). When the valve opens, the gas expands to the cell containing the solid adsorbent. After some time the equilibrium will be reached with the adsorbent at T_{oven} (temperature of the oven) and at P_{exp} (pressure after the expansion). From the mass balance (Annex B) the following expression is obtained

$$m_{GE} = V_{ref}\left(\rho_g(P_{ref}, T_{ref}) - \rho_g(P_{exp}, T_{ref})\right) + (V_c - V_s)\left(\rho_g(P_{exp_{n-1}}, T_{ov}) - \rho_g(P_{exp}, T_{ov})\right) + m_{GE_{n-1}}$$

Equation 7

The mass balance also considers the previous step as in each measurement an amount of gas remains in the cell.

Now, it is only necessary to choose the reference state to represent each isotherm. To determine the absolute amount adsorbed (q_t), a few more steps into the equation must be done.

The absolute state can be determined from the excess state (q_{ex}). They are related by

$$\mathrm{q_t = q_{ex} + V_p \rho_g}$$

Equation 8

Where V_p is the porous volume of the solid and ρ_g is the density of the gas under study in each experiment.

4.2.1 Error determination

The volumetric method is a standard method for measuring gas adsorption and is very simple to implement. However, if adsorption measurements are collected in a cumulative fashion without desorbing between each point, errors in the data can accumulate linearly. Therefore, it is important to identify all the major sources of error in a volumetric adsorption measurement.

The error estimation was performed using an equation accounting for multivariable and cumulative error

$$\sigma_X^2 = \left|\frac{\partial X}{\partial x_i}\right|^2 \sigma_{x_i}^2$$

Equation 9

where X represents any multivariable function, $\mathrm{x_i}$ represents the variable and $\sigma_{\mathrm{x_i}}^2$ the variable error. Using the mass balance equation determined previously, it was possible to determine the errors. The final equation and the previous step are shown on the annexe C. The results are shown together with the isotherms representations.

4.2.2 Carbon Dioxide Isotherms

There were performed three carbon dioxide isotherms at three different temperatures, 30ºC, 80ºC and 150ºC both on activated carbon, ANGUARD 5, and on MIL-53(Al) metal-organic framework,. The isotherms measured at 80ºC and 150ºC covered a pressure range from 0 to 15 bar while the 30ºC isotherm was measured in a pressure range from 0 to 10 bar. The results are shown below.

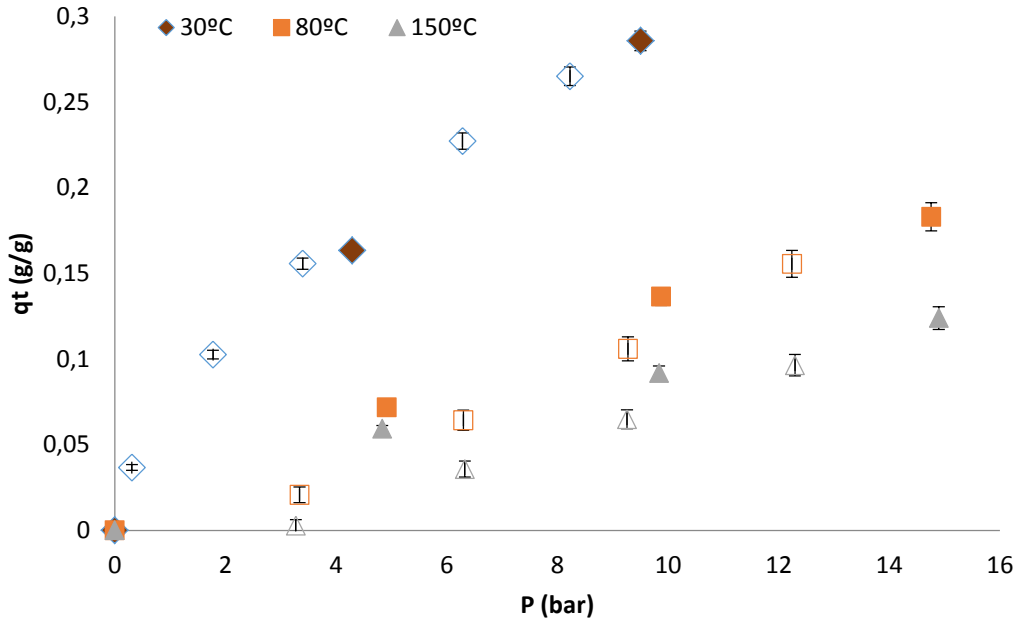


Figure 4.2 - Total amount adsorbed of carbon dioxide on ANGUARD 5 at 30ºC, 80ºC and 150ºC

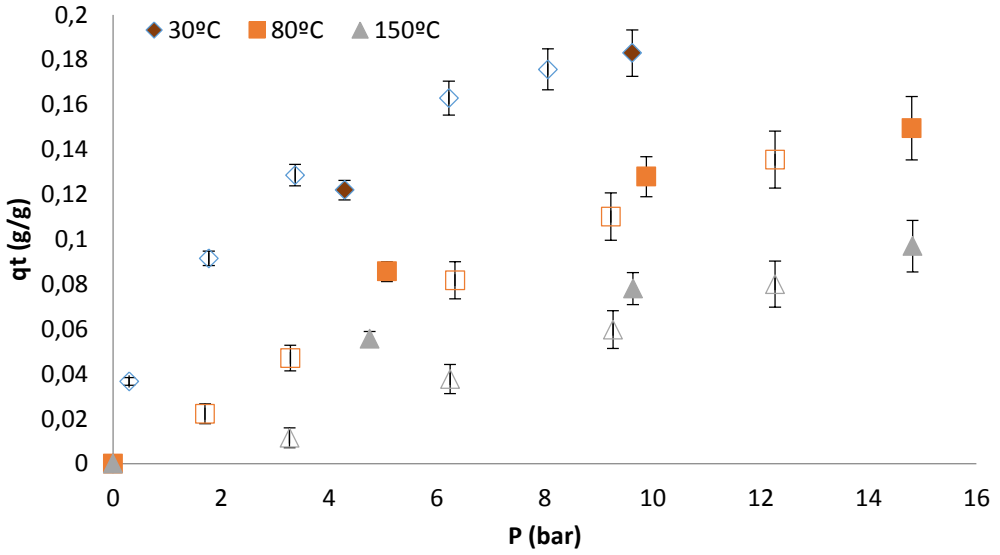


Figure 4.3 - Total amount adsorbed of carbon dioxide on MIL-53(Al) at 30ºC, 80ºC and 150ºC

It is possible to see that all isotherms, despite the temperature change, show a Type I behaviour, as it would be expected. Both materials used, ANGUARD 5 and MIL-53 (Al), are microporous materials that will provide type I isotherms. The isotherms also display a proper behaviour regarding the temperature since the isotherms are shown from top to bottom when the temperature increases. However the isotherms also show some deviation between adsorption and desorption points. This could be related to the unidirectional behaviour of the solenoid valves.

4.2.3 Nitrogen Isotherms

There was measured one nitrogen isotherm, at 50ºC on an activated carbon, ANGUARD 5, and on a metal-organic framework, MIL-53. The pressure range studied was 0 to 20 bar. The adsorption isotherms of N2 at 50ºC obtained is showed in Figure 4.3 for ANGUARD 5 and Figure 4.4 for MIL-53(Al)

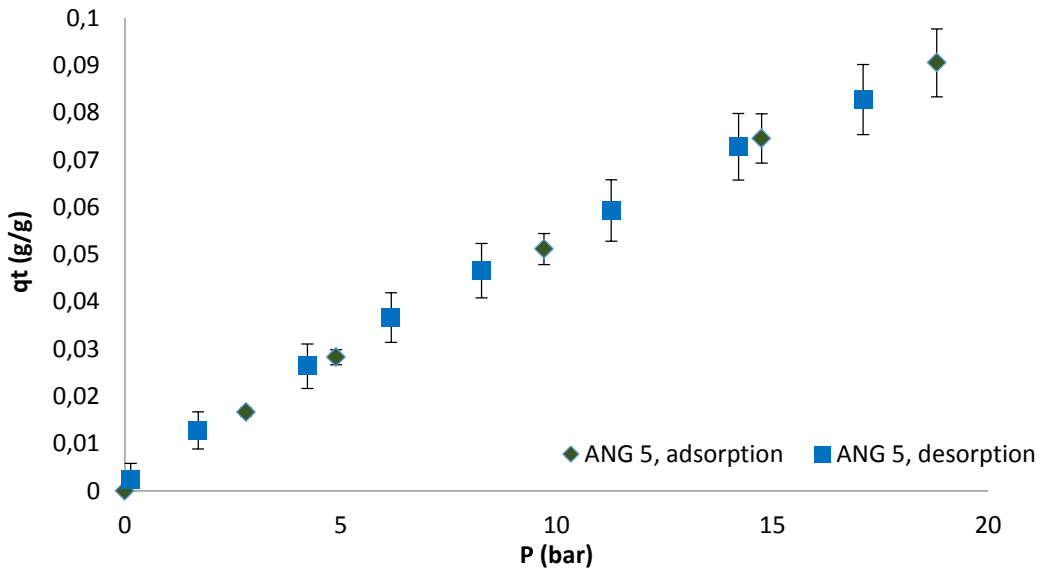


Figure 4.4 - Total amount adsorbed of nitrogen on ANGUARD 5 at 50ºC

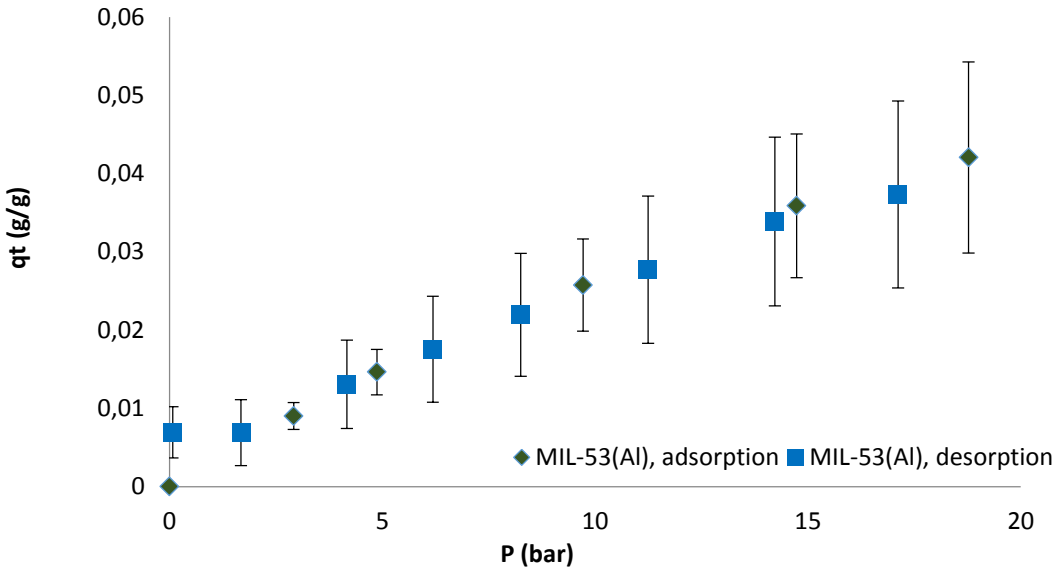


Figure 4.5 - Total amount adsorbed of nitrogen on MIL-53(Al) at 50ºC

It is possible to see that all isotherms, despite the temperature change, show a Type I behaviour, as it would be expected. Both materials used, ANGUARD 5 and MIL-53 (Al), are microporous materials that will provide type I isotherms.

4.3 Volumetric Data *versus* Gravimetric Data

After the measurement of the CO_2 and N_2 isotherms the obtained data was compared with the data previously obtained by the group in the gravimetric apparatus. The data obtained in the gravimetric apparatus for CO_2 isotherms does not correspond to the temperatures studied in this thesis apart from the CO_2 isotherm on MIL-53-Al at 80ºC. A model, the Sips model, whose parameters have been determined in said gravimetric equipment, was used. The N_2 isotherms were compared with experimental data from the gravimetric apparatus. The Sips model, as shown on equation 11, is a combination between Freundlich and Langmuir equations to allow the achievement of an improved fit at higher pressures. [44]

$$q_t = q_{ts}\frac{(bP)^{1/n}}{1+(bP)^{1/n}}$$

Equation 10

Where q_t is the amount adsorbed in mole per unit mass or volume, q_{ts} is the maximum amount adsorbed, b is the affinity constant and measure how strong the adsorbate molecule is attracted to a surface, P is the pressure and the parameter n characterizes the interaction between adsorbate/adsorbent and its magnitude increases with the heterogeneity of the system.

To perform the comparison between the experimental data obtained with the volumetric method and the gravimetric method the following parameters were used to determine the Sips model.

	ANGUARD 5	MIL-53 (Al)
q_s (g/g)	0,907	0,398
b_0(bar^{-1})	0,036	0,113
α	0,126	0,142
n_0	1,252	1,437
Q (J/mol)	19580	24998,09
T_0 (K)	299,1	303,163
R_g J/(mol.K)	8,314	8,314

Table 4.2 - Parameters used on Sips model

The affinity constant b and the parameter n can be written in function of the temperature as:

$$b = b_0 e^{\left[\frac{Q}{R_g T}\left(\frac{T_0}{T}-1\right)\right]}$$

Equation 11

$$\frac{1}{n} = \frac{1}{n_0} + \alpha\left(1 - \frac{T_0}{T}\right)$$

Equation 12

4.3.1 Carbon Dioxide Isotherms

ANGUARD 5

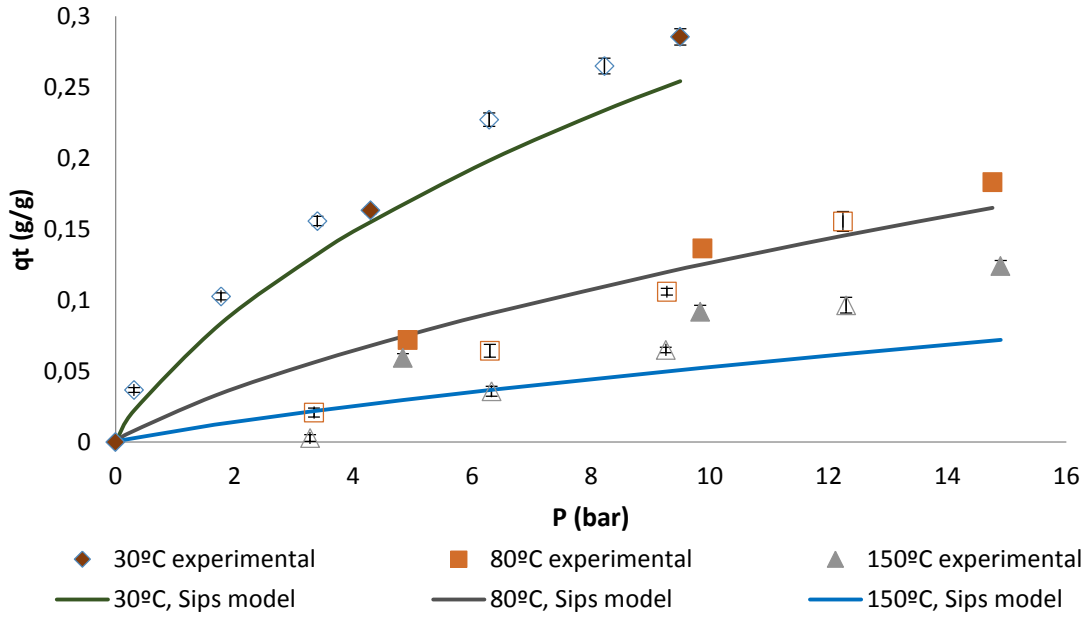


Figure 4.6 - Comparison between total amount adsorbed of carbon dioxide on ANGUARD 5 at 30ºC, 80ºC and 150ºC with data obtained with the Sips model

MIL-53(Al)

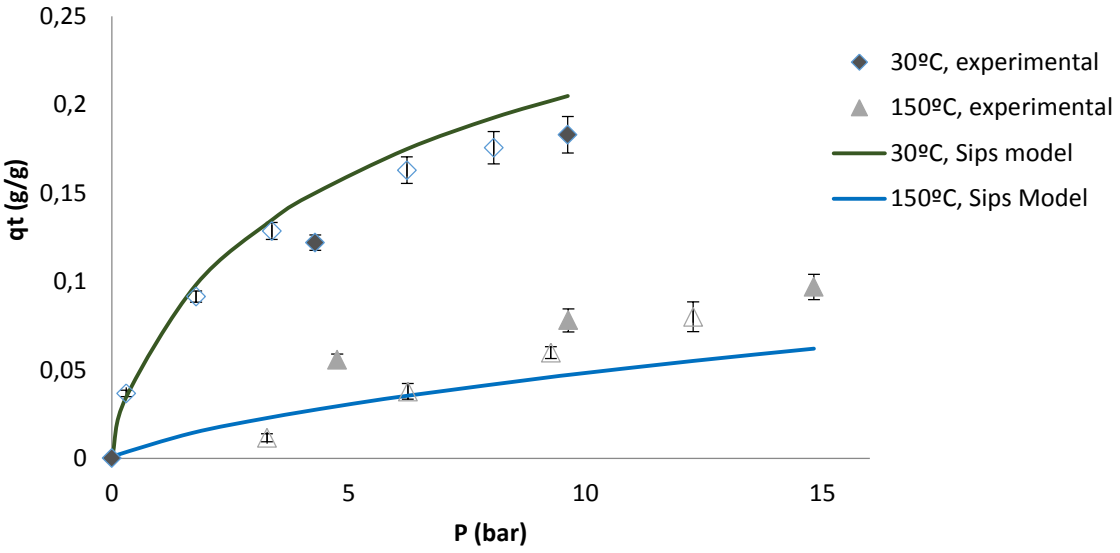


Figure 4.7 - Comparison between total amount adsorbed of carbon dioxide on MIL-53(Al) at 30ºC and 150ºC obtained experimentally with Sips model

The isotherm with MIL-53(Al) at 80ºC was compared with results taken simultaneously with this study.

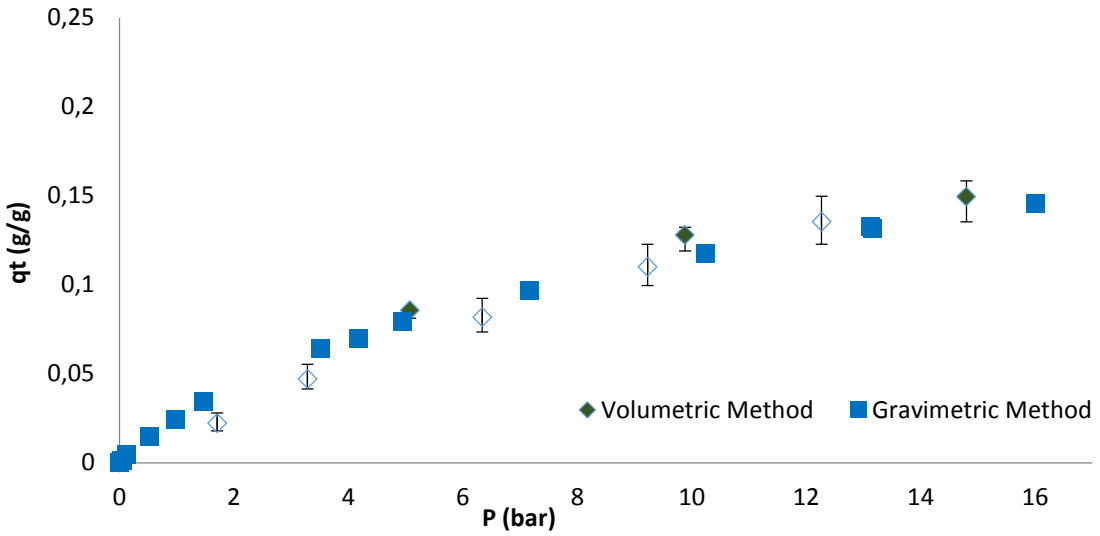


Figure 4.8 - Comparison between total amount adsorbed of carbon dioxide on MIL-53(Al) at 80ºC obtained experimentally with data obtained from the gravimetric apparatus

As can be observed from the previous figures, the experimental data obtained with the volumetric method tend to fit with the data obtained with the gravimetric method. At 30ºC and 80ºC the comparison shows great results, as the deviation between the volumetric and gravimetric data is minimal. However, as the temperature rises, the difference between the experimental results and the results of the model used increases. This is due to the fact that, as the temperature rises, the difference between the temperature inside and outside of the oven also increases. Also, this data was extrapolated from the parameters obtained from the fitting of the Sips isotherms from gravimetric method which can lead to some errors.

4.3.2 Nitrogen Isotherm

The nitrogen isotherms with ANGUARD 5 were compared with results already published. [19]. The isotherms with MIL-53(Al) were compared with results taken simultaneously with this study.

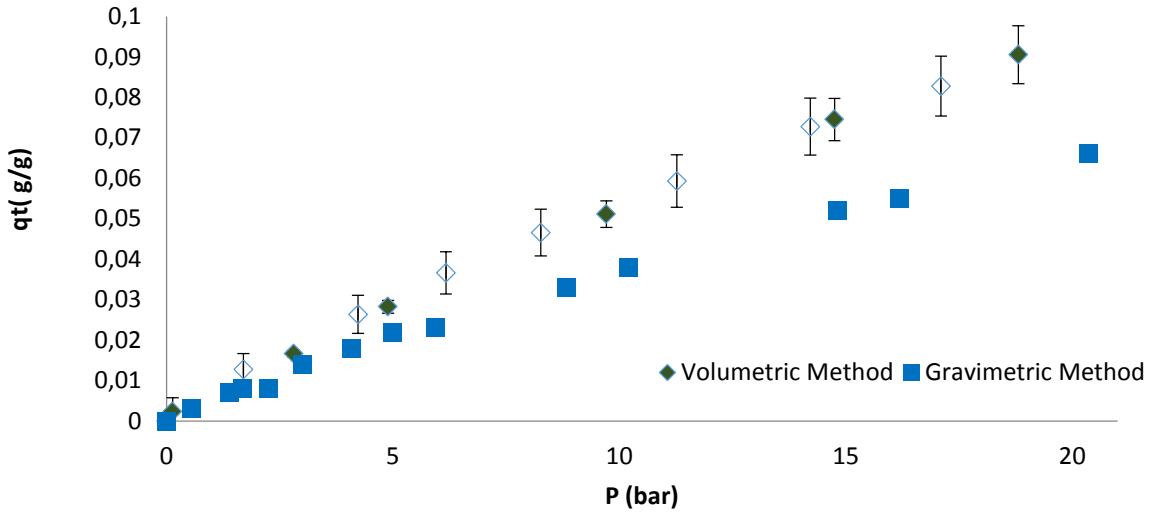


Figure 4.9 - Comparison between total amount adsorbed of nitrogen on ANGUARD 5 at 50ºC obtained experimentally with data obtained from the gravimetric apparatus

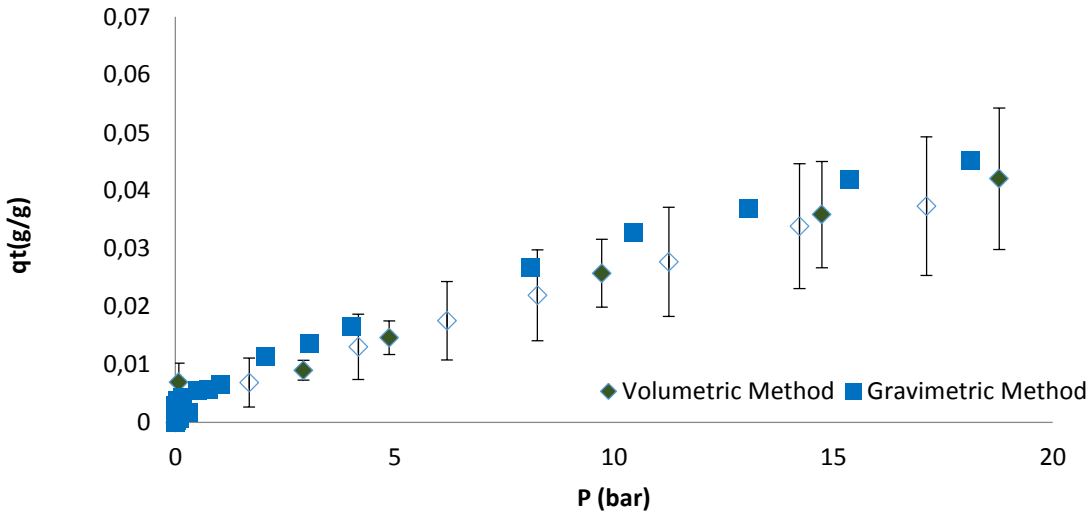


Figure 4.10 - Comparison between total amount adsorbed of nitrogen on MIL-53(Al) at 50ºC obtained experimentally with data obtained from the gravimetric apparatus

The volumetric data tend to fit with the gravimetric data. The comparison shows great results, as the deviation between the volumetric and gravimetric data is minimal.

5. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

5.1 Conclusions

The main objective of this thesis was to design and build a lab-scale volumetric adsorption unit. The unit was fully mounted at the group's lab, including the development of appropriate software for unit operation and monitorization. The unit allows the measurement of adsorption equilibrium data on two different adsorbent samples simultaneously.

After concluding the assembly of the volumetric unit, several adsorption equilibrium data was obtained, on previously studied adsorbent materials, in order perform the unit validation. For this purpose two different microporous materials were chosen, an activated carbon in the form of extrudates (ANGUARD 5 from Sutcliffe Speakman Ltd., UK) and a powdered MOF (MIL-53(Al) synthesized by BASF SE (Germany)). Carbon Dioxide and Nitrogen isotherms were measured on both adsorbents at different temperatures (30ºC, 80ºC and 150ºC for CO_2 and 50ºC for N_2) and pressure (0-15 bar for CO_2 and 0-20 bar for N_2). The isotherms obtained showed type I behaviour as expected.

The data obtained in the new volumetric unit was compared with the data previously obtained by the group in a magnetic suspension microbalance (gravimetric method). The results obtained by the volumetric method are in agreement with the gravimetric obtained data which demonstrates that the unit built is working properly. However, the results for the carbon dioxide isotherms at 150ºC show a significant deviation from data used for comparison. This may be due to the fact that this data was extrapolated from the parameters obtained from the fitting of the Sips isotherm performed employing the data obtained by gravimetric method. However, the difference between the temperature at the reference volume and the temperature on the oven also must be taken in account. This could also explain the deviations at higher temperatures, since the data obtained at lower temperatures are in better accordance with the data obtained in the gravimetric unit

5.2 Suggestions for Future Work

The development of the proposed ideas in this dissertation, together with the fruitful analysis of other studies, helped to identify potential areas for improvement and a number of issues that need to be investigated.

Regarding the volumetric unit itself, it would be interesting to add more lines in order allow measuring adsorption equilibrium data on more adsorbents samples in parallel. Among the most interesting features of the designed unit is the possibility of measuring adsorption isotherms at high temperatures. Therefore, measurement of adsorption equilibrium at high temperatures can be of great interest for, especially for modelling of adsorption based separation processes as Temperature Swing Adsorption.

Since in the designed unit the reference volume is outside the oven, there is a difference between its temperature and the adsorption cell temperature. Despite the fact that both temperatures are being measured, in the interface oven/environment a temperature gradient occurs. The influence of this gradient in the adsorption equilibrium measurements for high temperatures should be investigated. If this effect proves to be significant, the implementation of a temperature control apparatus for the reference volume (a thermal bath, for example) must be envisioned.

The solenoid valves purchased for this unit showed some problems. These valves only work on one way. When the reverse path is necessary, the valve cannot seal properly. It might be interesting considering changing these valves and replacing them for ball valves. If these ball valves are connected to a pneumatic actuator the valves could be controlled via LabVIEW as the solenoid valves employed at this point.

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7. ANNEXES

Annex A

Cell Volume Determination

In order to determine the cell volume for each line, the ideal gas law will be used.

$$PV = nRT \Leftrightarrow n = \frac{PV}{RT}$$

Equation 13

Upon expansion the total volume is the sum of the reference volume and the cell volume.

$$V_t = V_{ref} + V_c$$

Equation 14

When combine the previous equation with the ideal gas law we have,

$$V_t = V_{ref} + V_c$$

$$\frac{P_f V_t}{RT_f} = \frac{P_{r,i} V_{ref}}{RT_{ref}} + \frac{P_{c,i} V_c}{RT_{c,i}}$$

$$\frac{P_f V_t}{T_f} = \frac{P_{r,i} V_{ref}}{T_{ref}} + \frac{P_{c,i} V_c}{T_{c,i}}$$

$$\frac{P_f V_{ref}}{T_f} + \frac{P_f V_c}{T_f} = \frac{P_{r,i} V_{ref}}{T_{ref}} + \frac{P_{c,i} V_c}{T_{c,i}}$$

$$\frac{P_f V_c}{T_f} - \frac{P_{c,i} V_c}{T_{c,i}} = \frac{P_{r,i} V_{ref}}{T_{ref}} - \frac{P_f V_{ref}}{T_f}$$

$$V_c \left(\frac{P_f}{T_f} - \frac{P_{c,i}}{T_{c,i}} \right) = V_{ref} \left(\frac{P_{r,i}}{T_{ref}} - \frac{P_f}{T_f} \right)$$

$$V_c = V_{ref} \frac{\left(\frac{P_{r,i}}{T_{ref}} - \frac{P_f}{T_f} \right)}{\left(\frac{P_f}{T_f} - \frac{P_{c,i}}{T_{c,i}} \right)}$$

Equation 15

Annex B

Mass balance for determination of the gas amount adsorbed

The initial considerations are:

$$\begin{cases} V_i = V_{ref} \\ V_f = V_{ref} + V_c - V_s \end{cases}$$

Equation 16

Considering the mass of gas on the previous moment of the expansion,

$$\begin{cases} m_i = m^*_{ref} + m^*_{c_{n-1}} + m_{ads_{n-1}} \\ m_f = m_{ref} + m_c + m_a \end{cases}$$

Equation 17

As there are no changes on the mass values,

$$m_i = m_f$$

$$m^*_{ref} + m^*_{c_{n-1}} + m_{ads_{n-1}} = m_{ref} + m_c + m_a$$

$$m_a = m^*_{ref} + m^*_{c_{n-1}} - m_{ref} - m_c + m_{ads_{n-1}}$$

Equation 18

In fact, this equation does not determine the adsorbed mass but instead the Gibbs surface excess mass. The surface excess is the difference between the amount of a component actually present in the system, and that which would be present in a reference system if the bulk concentration in the adjoining phases were maintained up to a chosen geometrical dividing force.

So, changing the name and using the real gases equations, we have,

$$m_{GE} = \frac{MV_{ref}P^*_{ref}}{RT^*_{ref}Z_{ref}} + \frac{M(V_c - V_s)P^*_{exp_{n-1}}}{RT^*_{ov_{n-1}}Z_{exp}} - \frac{MV_{ref}P_{exp}}{RT_{ref}Z_{exp}} - \frac{M(V_c - V_s)P_{exp}}{RT_{ov}Z_{exp}} + m_{GE_{n-1}}$$

$$m_{GE} = V_{ref}\left(\frac{MP^*_{ref}}{RT^*_{ref}Z_{ref}} - \frac{MP_{exp}}{RT_{ref}Z_{exp}}\right) + (V_c - V_s)\left(\frac{MP^*_{exp_{n-1}}}{RT^*_{ov_{n-1}}Z_{exp}} - \frac{MP_{exp}}{RT_{ov}Z_{exp}}\right) + m_{GE_{n-1}}$$

$$m_{GE} = V_{ref}\left[\rho_g(P_{ref}, T_{ref}) - \rho_g\left(P_{exp}, T_{ref}\right)\right] + (V_c - V_s)\left[\rho_s\left(P_{exp,n-1}, T_{ov,n-1}\right) - \rho_g\left(P_{exp}, T_{ov}\right)\right] + m_{ex,n-1}$$

Equation 19

Annex C

Error determination

As it is said on chapter 4, in order to determine the error in each measurement, it was assumed that the error is multivariable and cumulative.

$$\sigma_X^2 = \left|\frac{\partial X}{\partial x_i}\right|^2 \sigma_{x_i}^2$$

Equation 20

As the calculations for the total amount adsorbed *qt* do not impose any problems, the main concern relies on the Gibbs excess mass equation.

$$m_{GE} = V_{ref}\left[\rho_g(P_{ref}, T_{ref}) - \rho_g\left(P_{exp}, T_{ov}\right)\right] + (V_c - V_s)\left[\rho_s\left(P_{exp,n-1}, T_{ov,n-1}\right) - \rho_g\left(P_{exp}, T_{ov}\right)\right] + m_{ex,n-1}$$

$$m_{GE} = V_{ref}\left(\frac{MP_{ref}^*}{RT_{ref}^* Z_{ref}} - \frac{MP_{exp}}{RT_{ov} Z_{exp}}\right) + (V_c - V_s)\left(\frac{MP_{exp_{n-1}}^*}{RT_{ov_{n-1}}^* Z_{exp}} - \frac{MP_{exp}}{RT_{ov} Z_{exp}}\right) + m_{GE_{n-1}}$$

Equation 21

Since this is multivariable equation simpler steps were performed. First, the equation was separated in several quantities.

$$m_{ex} = A + B + C + D + E + F + m_{ex,n-1}$$

Equation 22

Where,

$$A = V_{ref} \cdot \frac{M}{R} \cdot \frac{P_{ref}}{T_{ref} Z_{ref}}$$

$$B = -V_{ref} \cdot \frac{M}{R} \cdot \frac{P_{exp}}{T_{ov} Z_{ov}}$$

$$C = V_c \cdot \frac{M}{R} \cdot \frac{P_{exp,n-1}}{T_{ov} Z_{n-1}}$$

$$D = -V_c \cdot \frac{M}{R} \cdot \frac{P_{exp}}{T_{ov} Z_{ov}}$$

$$E = -V_s \cdot \frac{M}{R} \cdot \frac{P_{exp,n-1}}{T_{ov} Z_{n-1}}$$

$$F = V_s \cdot \frac{M}{R} \cdot \frac{P_{exp}}{T_{ov} Z_{ov}}$$

Equation 23

Now, using the multivariable and cumulative error equation, we can obtained the following equations.

$$\sigma_A^2 = \left|\frac{\delta A^2}{\delta xi}\right| \cdot {\sigma_{xi}}^2 = \left(\frac{\delta A}{\delta V_{ref}}\right)^2 \cdot \sigma_{V_{ref}}^2 + \left(\frac{\delta A}{\delta P_{ref}}\right)^2 \cdot \sigma_P^2 + \left(\frac{\delta A}{\delta T}\right)^2 \cdot \sigma_T^2$$

$$= \left[\frac{M}{R} \cdot \frac{P_{ref}}{T_{ref} Z_{ref}}\right]^2 \cdot \sigma_{V_{ref}}^2 + \left[V_{ref} \cdot \frac{M}{R} \cdot \frac{1}{T_{ref} Z_{ref}}\right]^2 \cdot \sigma_P^2 + \left[-V_{ref} \cdot \frac{M}{R} \cdot \frac{P_{ref}}{{T_{ref}}^2 Z_{ref}}\right]^2 \cdot \sigma_T^2$$

Equation 24

$$\sigma_B^2 = \left|\frac{\delta B^2}{\delta xi}\right| \cdot {\sigma_{xi}}^2 = \left(\frac{\delta B}{\delta V_{ref}}\right)^2 \cdot \sigma_{V_{ref}}^2 + \left(\frac{\delta B}{\delta P_{exp}}\right)^2 \cdot \sigma_P^2 + \left(\frac{\delta B}{\delta T}\right)^2 \cdot \sigma_T^2$$

$$= \left[-\frac{M}{R} \cdot \frac{P_{exp}}{T_{ov} Z_{ov}}\right]^2 \cdot \sigma_{V_{ref}}^2 + \left[-V_{ref} \cdot \frac{M}{R} \cdot \frac{1}{T_{ov} Z_{ov}}\right]^2 \cdot \sigma_P^2 + \left[-V_{ref} \cdot \frac{M}{R} \cdot \frac{P_{exp}}{{T_{ov}}^2 Z_{ov}}\right]^2 \cdot \sigma_T^2$$

Equation 25

$$\sigma_C^2 = \left|\frac{\delta C^2}{\delta xi}\right| \cdot {\sigma_{xi}}^2 = \left(\frac{\delta C}{\delta V_c}\right)^2 \cdot \sigma_{V_c}^2 + \left(\frac{\delta C}{\delta P_{exp,n-1}}\right)^2 \cdot \sigma_P^2 + \left(\frac{\delta C}{\delta T}\right)^2 \cdot \sigma_T^2$$

$$= \left[\frac{M}{R} \cdot \frac{P_{exp,n-1}}{T_{ov} Z_{n-1}}\right]^2 \cdot \sigma_{V_c}^2 + \left[V_c \cdot \frac{M}{R} \cdot \frac{1}{T_{ov} Z_{n-1}}\right]^2 \cdot \sigma_P^2 + \left[V_c \cdot \frac{M}{R} \cdot \frac{P_{exp,n-1}}{{T_{ov}}^2 Z_{n-1}}\right]^2 \cdot \sigma_T^2$$

Equation 26

$$\sigma_D^2 = \left|\frac{\delta D^2}{\delta xi}\right| \cdot {\sigma_{xi}}^2 = \left(\frac{\delta D}{\delta V_c}\right)^2 \cdot \sigma_{V_c}^2 + \left(\frac{\delta D}{\delta P_{exp}}\right)^2 \cdot \sigma_P^2 + \left(\frac{\delta D}{\delta T}\right)^2 \cdot \sigma_T^2$$

$$= \left[-\frac{M}{R} \cdot \frac{P_{exp}}{T_{ov} Z_{ov}}\right]^2 \cdot \sigma_{V_c}^2 + \left[-V_c \cdot \frac{M}{R} \cdot \frac{1}{T_{ov} Z_{ov}}\right]^2 \cdot \sigma_P^2 + \left[V_c \cdot \frac{M}{R} \cdot \frac{P_{exp}}{{T_{ov}}^2 Z_{ov}}\right]^2 \cdot \sigma_T^2$$

Equation 27

$$\sigma_E^2 = \left|\frac{\delta E^2}{\delta xi}\right| \cdot {\sigma_{xi}}^2 = \left(\frac{\delta E}{\delta V_s}\right)^2 \cdot \sigma_{V_s}^2 + \left(\frac{\delta E}{\delta P_{exp,n-1}}\right)^2 \cdot \sigma_P^2 + \left(\frac{\delta E}{\delta T}\right)^2 \cdot \sigma_T^2$$

$$= \left[-\frac{M}{R} \cdot \frac{P_{exp,n-1}}{T_{ov} Z_{n-1}}\right]^2 \cdot \sigma_{V_s}^2 + \left[-V_s \cdot \frac{M}{R} \cdot \frac{1}{T_{ov} Z_{n-1}}\right]^2 \cdot \sigma_P^2 + \left[V_s \cdot \frac{M}{R} \cdot \frac{P_{exp,n-1}}{{T_{ov}}^2 Z_{n-1}}\right]^2 \cdot \sigma_T^2$$

Equation 28

$$\sigma_F^2 = \left|\frac{\delta F^2}{\delta xi}\right| \cdot {\sigma_{xi}}^2 = \left(\frac{\delta F}{\delta V_s}\right)^2 \cdot \sigma_{V_s}^2 + \left(\frac{\delta F}{\delta P_{exp}}\right)^2 \cdot \sigma_P^2 + \left(\frac{\delta F}{\delta T}\right)^2 \cdot \sigma_T^2$$

$$= \left[\frac{M}{R} \cdot \frac{P_{exp}}{T_{ov} Z_{ov}}\right]^2 \cdot \sigma_{V_s}^2 + \left[V_s \cdot \frac{M}{R} \cdot \frac{1}{T_{ov} Z_{ov}}\right]^2 \cdot \sigma_P^2 + \left[-V_s \cdot \frac{M}{R} \cdot \frac{P_{exp}}{{T_{ov}}^2 Z_{ov}}\right]^2 \cdot \sigma_T^2$$

Equation 29

In the end, the error on each measurement is,

$$\sigma_{m_{ex}}^2 = \sigma_A^2 + \sigma_B^2 + \sigma_C^2 + \sigma_D^2 + \sigma_E^2 + \sigma_F^2 + \sigma_{m_{ex,n-1}}^2$$

Equation 30